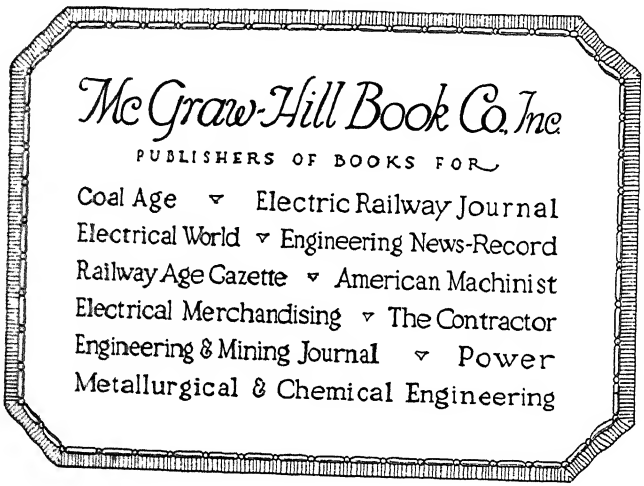

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COAL GAS RESIDUALS

BY

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DEDICATED TO THE MEMORY OF

WALTHER FELD

of whom nothing of greater praise can be said than by repeating the following lines which appeared in "Die Chemische Industrie," published in Germany, namely:

"The barium industry as well as industries connected with tar and ammonia must thank him for the new paths which he has broken, and in the history of the development of German chemical industries the life work of Walther Feld must for all time remain an imperishable page of fame."

PREFACE TO SECOND EDITION

CONDITIONS arising during this period when there is a general patriotic endeavor to supply the War Department with the many products needed to carry the war to a successful issue, have necessitated the addition of certain special features to this book: hence the new edition.

The important additions are the treatment of the process of distillation and some general information on tar products to the chapter on tar; additional information on the product derived from spent oxide in the chapter on cyanogen; data on the production of nitric acid to the chapter on ammonia; additional data to the chapter on naphthalene; some new material on the production of benzol and toluol; and a chapter on the manufacture of sulphuric acid when spent oxide is used as a base.

The test for cyanogen has been revised so that the chemist engaged in this work finds it simple and practical.

I wish to thank the friends who have called attention to typographical errors in the previous edition. These have been corrected.

I trust that this revised edition may find as much favor among operators as did the former one.

FREDERICK H. WAGNER

BALTIMORE, MD., November, 1917

PREFACE TO FIRST EDITION

THE lack of general information in concise form covering the various methods of securing the residuals pertaining to the carbonization of coal, and the necessity of calling attention to the waste of our natural resources in so many instances, was the incentive leading to the writing of the following pages. All of the residuals except coke are treated, the latter product being reserved for a separate volume, and in presenting the Feld theory and practice to the coal gas producer, as well as to the coke oven operator, I am taking the liberty of quoting the two appended letters, first by Camillo J. Guttmann, of London, which appeared in the Gas World on July 18, 1914, and the second by W. R. Ormandy from the Gas World of August 8, 1914.

The first letter says:

"The advantages of oil over coal as a source of power for many purposes, but particularly for naval purposes, have lately beeen so vigorously canvassed and so exhaustively discussed by engineering experts, that there is now no purpose in dilating upon them. In view of the fact that, whether for good or ill, the die has now been cast in favor of oil, and that the nation (English nation) has already committed itself to far-reaching schemes of foreign exploitation, it becomes much more pertinent at the moment to consider what resources we have for securing our supplies at home; for besides the more obvious advantages, there are others hardly less important in finding our sources of supply in this country.

In articles which have recently appeared in the Press, public attention was directed to this aspect of the question, and to the possibility of producing oils for the Navy from bituminous coal, shale, peat, or even sewage matter. These articles mainly drew attention to the del Monte and similar processes of obtaining motor spirit and fuel oil from coal. While these processes will certainly promote the solution of the oil fuel problem, they are somewhat dependent for their ultimate fruition on the successful creation of a market for their residual product — a semi-fuel for household and like purposes.

These interesting articles, however, omitted to mention one process which, to my mind, whether alone or in combination with other methods,

opens up a wide vista of possibilities in this connection. I refer, as most experts will have guessed, to the process perfected by the late Walther Feld. This process without the intervention of any other, produces not only fuel oils, but, at the same time, and in one operation, a pitch containing practically no free carbon (in other words, precisely the pitch that is now in ever growing demand for road-making and other purposes), a benzol which is valuable as a substitute for petrol, and, finally, the usual yield of ammonium sulphate. This last is produced direct by a beautifully simple process which entirely obviates the necessity of purchasing or manufacturing sulphuric acid.

The general introduction of this process in coke-oven plants and in gas-works throughout the country would, apart from the economy in working and prime costs, greatly assist in providing a natural, national and adequate reserve of oil fuel, and is, therefore, worthy of earnest consideration jointly with other processes direct towards this end.

It should be noted that the success of the Feld process is not in any way dependent on the sale of a residual product, constituting, as it does, an improvement on existing processes in by-product recovery.

Our agricultural interests would derive all the advantage of a more rational production of ammonium sulphate. The fertility of land may, in many cases, be trebled by the judicious use of this, one of the most generally valuable of our artificial manures. Ammonium sulphate is now recognized to be so necessary that its use has almost become a criterion of the progress of agriculture, and of the degree of a country's enlightenment.

The writer recently had the privilege of inspecting a trial Feld plant installed at the works of one of the foremost Westphalian coal and iron firms, and intended to deal with the gases from a battery of coke-ovens with a daily capacity of 800, and ultimately 1600 tons of coal. This plant is, I understand, the first of several which are on order, and in the writer's opinion, represents the first step by which Germany will ultimately become largely independent of foreign oil for her Navy, and of petrol for her motor-propelled vehicles.

The above considerations are not intended to put forward the Feld process as a panacea for the fuel problem, but to show that the available field is a broad one, and that the Feld process must necessarily play an important part in any future developments.

It will be seen that the present needs of our Admiralty furnish the Government with a rare opportunity for combining the solution of a departmental economy with a new industrial departure influencing our national economy, and which will not only increase our power for offensive defence, but — and this is interesting — enhance our power for passive resistance just where it is weakest, by reinforcing our home supplies of food.

It is much to be hoped that our rulers will show themselves sufficiently enlightened to embrace this opportunity and, what is quite as essential, embrace it promptly and vigorously."

The second communication, that from Mr. W. R. Ormandy, says:

"From the correspondence which has been taking place in The Gas World it is quite obvious that the problem which Mr. Feld set out to solve is not realized by all readers. No doubt from time to time descriptions of Feld plant and processes have appeared in these columns; but in view of the increased attention which is now being devoted towards the better utilization of the national fuel resources it might not be out of place to describe briefly the general principles which Mr. Feld enunciated.

Regarded from a scientific standpoint, even the most modern methods of utilizing fuel are carried out in a primitive and, in most cases, barbarous manner. In coke-oven and gas-works practice coal is distilled and the heterogeneous products of such distillaton are condensed together into an abominable mixture upon which subsequently much time, skill, fuel and capital has to be spent to bring about even a partial separation of the tarry mass into its separate constituents. Maybe Mr Feld was not the first to realize the waste that was involved in such a process and to point out how much more rational and economical it would be to separate the various constituents of the distillate by means of an adequate system of fractional cooling and washing. On the other hand, he was undoubtedly the first to make this problem a life-work, and to set out to devise apparatus and to work out reactions to overcome the difficulties with which every step in this great problem was beset. A comparatively superficial examination of the problems involved showed the impossibility of dealing with the complicated products of the distillation of coal in an adequate manner. Making use of liquid reagents and the utilization of insoluble reagents in suspension brought with it the necessity of devising some new form of washing apparatus wherein such solid suspensions could be used continuously and efficiently. This led to the evolution of the Feld washer, which alone rendered possible the utilization of many of the reactions which had subsequently to be made use of. In spite of the many difficulties under which he labored, Mr. Feld succeeded in perfecting and proving the suitability of the intensive type of centrifugal washer, and lived long enough to find the principles involved therein adapted by a large number of makers who flooded the markets with modifications as close to the original as the law permitted.

The next stage of development necessitated an intimate knowledge of the vapor tension and vapor pressure of solutions of gases and of oils. Much of this was non-existent, and it necessitated a vast amount of work

before a basis was available upon which to build the superstructure of the new process. Instead of cooling the gases from whatever form of distilling apparatus was being employed, these were kept at such a temperature that no deposition of even the most easily condensable of them took place before the products were allowed to enter the first washer. So far as regards dealing with the oils, the principle involved was similar throughout, namely, to reduce the temperature by stages in a number of washers, so that the gas was cooled in any one stage to such a temperature as allowed of condensation of whatever product was desired in that stage. Thus, in the plant visited by the writer, in the neighborhood of Teplitz, in Austria, where the products of distillation of a large number of by-product coke ovens distilling brown coal were being treated, the first washer was kept at such a temperature as permitted only of the condensation therein of pitches and tars and oils boiling above the temperature of 240 degrees C. The fluid tar running away from the bottom of the first cooling washer was allowed to cool and re-circulated, by means of a pump, through this washer at such a rate as enabled the necessary reduction in temperature to take place. In each of the subsequent coolers a similar chain of operations took place. It is obvious that it is possible by increasing or diminishing the number of coolers and by varying the rate of cooling, to obtain oils from any one washer boiling between any desired range of temperatures. In this wise, at Teplitz tar, heavy oil, and light oil were separated free from water and ammonia. By this time the temperature of the gases has been brought so low that the water vapor contained therein is on the verge of condensing. By using the counter-current system and allowing the gases to meet a stream of water in the Feld washer it is possible to reduce the temperature of the outgoing gas to about 60 degrees C., and yet to have water leaving the washer at such a temperature that no appreciable amount of ammonia remains therein. By similar ingenious means the temperature of the gases was lowered still further without loss of ammonia until a product was left containing the whole of the ammonia and so little water that it was possible to recover the ammonia as sulphate free from tar and coloring matter by means of some of the many reactions which Feld worked out for this purpose.

It would lead us too far at this point to go into the details regarding the recovery of cyanogen, but it is worth pointing out that the Feld system of fractional cooling permits of the removal of cyanogen at a temperature and under conditions which prevent the formation of the sulphur compounds of cyanogen, which lead to such heavy losses of this valuable material, in operations carried out under the old régime. The cooling of the gases to a degree which permits of the removal of the ammonia salts still permits of the benzene compounds remaining in the form of vapor, and subsequent washing in a final Feld washer with heavy oil results in

the recovery of practically the whole of the benzene group boiling below 140 degrees C. in a form which permits of their recovery in great purity with the minimum of labor and expense.

The subject of the recovery of the ammonia as sulphate at the expense of the sulphur contained in the gas with the ammonia has been in the public eye to such an extent during the last few years that the work of Feld in this direction has no doubt caused the general public to overlook the service which he has rendered by not only pointing out better theoretical lines upon which to attack the great problem of dealing with coal tar distillates, but in proving that such theoretical methods were well within the practical province.

There is no doubt that the immediate future will witness great advances in the more intelligent utilization of our fuel resources and such improvement is bound to be accompanied by the production of increased amounts of both volatile and heavy oils. It is almost impossible to conceive that such advances can take place without benefiting in a large degree from the pioneer work carried out by Mr. Feld, and thus far Mr. Guttmann is more than justified in associating Mr. Feld's name with fuel oil from national sources."

The author would greatly appreciate any suggestions from the readers of this book with the view of extending its usefulness in ensuing editions, and in thus keeping its contents abreast of any developments made in this field of conservation and industry.

FREDERICK H. WAGNER

BALTIMORE, MD., August, 1914.

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COAL GAS RESIDUALS

INTRODUCTORY

A hundred years of development have passed since Murdoch's discoveries permitted the lighting of the city of London with coal gas, and these years have placed gas lighting in the forefront of industrial progress, while the history of these years plainly shows how the proper utilization of by-products can revolutionize the magnitude of an industry. The early years of coal carbonization could depend upon no, or but very little, assistance from by-product sales in the matter of cheapening the cost of production, and not until the aid of modern chemistry was called in, did the production of residuals make any appreciable change in this condition.

The recovery of residuals is a very important conservation of resources, and it forms one of the principal means of revenue to the coal-gas producer, the sale of these residuals reducing the cost of gas production in a degree corresponding to the efficiency of the recovery methods adopted and the market value of the product.

The principal residuals recovered today are tar, naphthalene, cyanogen, ammonia, and in the case of coke-oven gas, also benzol by a direct recovery method, and they will be treated in this consecutive order in the following pages. The recovery of benzol is confined almost entirely to the coke-oven plant, where a direct method of recovery is adopted, and to the tar distiller, benzol being one of the most valuable of tar constituents. While the recovery of naphthalene cannot exactly be termed one of profit in a pecuniary sense at present, the removal of a certain portion from the gas is of distinct advantage, and the methods adopted for its removal will, therefore, be given.

The gas produced during the carbonization of coal is a mixture of fixed gases, vapors of various kinds, and, at times,

also globules of liquids, which are held in suspension, and are thus carried forward by the gas; these gases and vapors also carry forward some solid carbon in the shape of dust.

The principal fixed gases are hydrogen, H_2; methane, CH_4, also known as "marsh" gas; ethane, C_2H_6; propane, C_3H_8, butane, C_4H_{10}; ethylene, C_2H_4; small amounts of butylene, C_4H_8; propylene, C_3H_6; acetylene, C_2H_2; carbon dioxide, CO_2; carbon monoxide, CO; hydrogen sulphide, H_2S; nitrogen, N_2; oxygen, O_2; and ammonia, NH_3; while the principal vapors in the mixture are benzol, C_6H_6; toluol, $C_6H_5CH_3$; xylol, $C_6H_4(CH_3)_2$; carbon disulphide, CS_2; and aqueous vapors. These latter vapors are those of substances which become liquid at ordinary temperatures, but the vapors of naphthalene, $C_{10}H_8$, phenols, etc., are those of substances which become solid at ordinary temperatures, and must, therefore, be subjected to a special treatment.

As will be seen later, some of these constituents are of inestimable value to the coal-gas producer, and consequently the treatment of the gas after it is produced in the carbonizing plant, is of great importance; this treatment should not only consist of a method of cooling the gas, and thus condensing and precipitating the vapors as a fluid, but the method of treatment should be such as to retain in the gas those valuable illuminating constituents which may be lost to a greater or lesser extent in the usual condensing plant, and thus the Feld system, which embraces successive cooling with a fractionation of the products, appears most attractive from the standpoint of efficiency and simplicity.

The usual condensing system in coal-gas practice embraces the use of a primary condenser, exhauster, tar extractor, secondary condenser, and ammonia washer, the tar, together with quite an amount of illuminants, being thus removed in a great measure by cooling, while in the Feld system the gas is not cooled below the point where any volatile hydro-carbons are precipitated or absorbed by the effluent, the tar being fractionated in three washers into pitch, heavy oils, and middle or light oils, and the gas is treated for cyanogen, combined hydrogen sulphide and ammonia, naphthalene, and finally benzol, the entire process being carried out in Feld vertical centrifugal washers, as shown in diagram A.

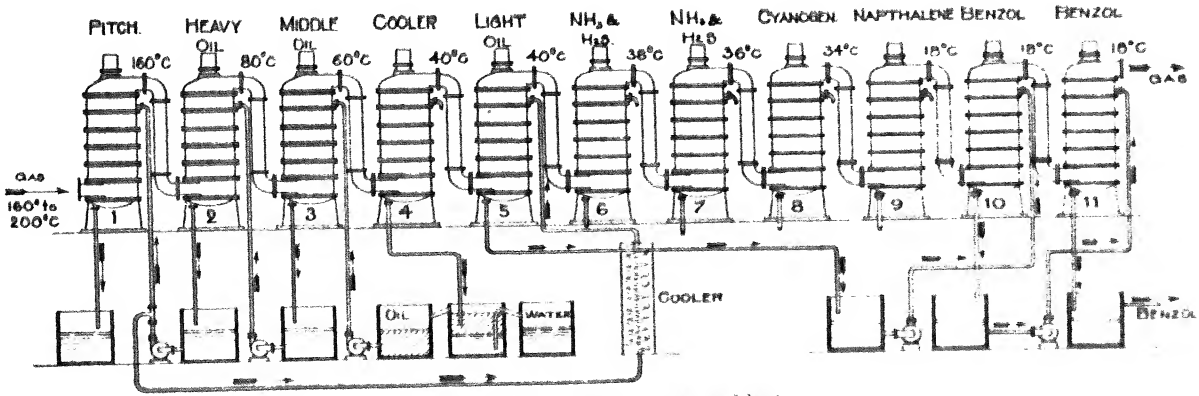


Diagram A Feld Condensing Plant

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As will be seen from Diagram A, the entire condensing plant consists of eleven washers, the first, or pitch washer operating at a temperature of from 160° to 200° C., the gas being kept at this temperature in its progress from the hydraulic main by insulating both the main and the pipe connections, or by the application of external heat, heavy oils from washer (2) being pumped into washer (1), where they are used as the active pitch-extracting medium.

Washer (2) removes the heavy oils, and it is operated at a temperature of from 160° to 80° C., all operating temperatures being determined from the actual dew point of the gas for the constituent to be removed, the extracting medium being the middle oils from washer (3).

Washer (3) removes the middle oils, due to contact between the gas and the oils separated by cooling in washer (4), this cooling being effected by bringing the gas into intimate contact with water, the effluent from washer (4) being run into a separating tank where the oil is separated from the water by specific gravity.

The light oils are removed in washer (5), where the gases are washed by means of heavy oils which are previously cooled in a special cooler, these light oils being run into a reservoir from whence they are pumped into the first benzol washer.

The washers for ammonia and hydrogen sulphide operate under a temperature of from 40° to 36° C., the hydrogen sulphide being combined with the ammonia in these washers with the consequent formation of ammonium sulphate, while the cyanogen washer operates at about 36° to 34° C.

The naphthalene is removed in washer (9) at a temperature of about 18° C., while washers (10) and (11) serve to extract the benzol and its homologues, the partially saturated oil coming from washer (10) being pumped into washer (11).

For the complete theory of condensation the reader is referred to "The Cleaning of Blast-Furnace Gases,"[1] only such portions of this theory as are applicable to the removal of tars and oils being given in the following chapters.

The usual method of condensation as practised in America

[1] Published by the McGraw-Hill Book Co., Inc., New York.

has as its natural result the cooling of the gas and, in so doing, the removal of those constituents which cannot remain permanently in the gas without fouling the purifying apparatus and the distributing system. This condensation starts as soon as the gas leaves the mouthpiece and enters the ascension or stand pipe delivering the gas to the hydraulic main, and it has been estimated that from 30 to 50 per cent of all condensible constituents are deposited in this main.

Heavy tars are thus deposited in the hydraulic main, and these should be removed as quickly as possible because their presence acts as an absorbent upon the illuminants, and thus reduces the candle-power of the gas. All subsequent condensation should proceed slowly in order to retain as many of the hydro-carbons in the gas as is possible, because sudden chilling not only removes these valuable constituents, but it also causes the deposition of some of them in the shape of naphthalene, with resultant stoppages.

The tar produced from coal gas is one of its most important residuals, and while it is used to some extent in its original form, it finds its most important application in the arts, where it forms the basis of aniline color production, 900 different colors and shades being listed as coming from tar, these being produced by distilling the tar in tar stills and, after a certain temperature has been reached, water-like oils result, these oils being the base of all of the beautiful coal-tar colors. Carbolic acid, naphthalene, anthracene, and benzol are also produced in like manner, and each of these constituents in turn produce a long series of other products. By treating anthracene we produce alizarin, one of the most valuable coloring matters, and which forms the base of indigo. Many blue dyes in early days were produced from the juice of the indigo plant, native to India, which juice, when exposed to the atmosphere, oxidized and precipitated indigo.

Indian indigo is still used to a great extent in the dyeing industry, but the blues produced from coal-tar are rapidly displacing it. The alizarin produced from coal-tar is identical in chemical composition and coloring properties with madder, and this has become a very valuable commercial product.

Substances termed mordants by dyers, owing to their fixing qualities, are mixed with the true coloring matter, and are thus employed as vehicles for the latter. By adding the mordant alumina to alizarin, red dyes result, and by adding the mordant iron, darker tones are produced, and by adding chrome the resultant colors are violet.

Chemists are able to split up quinine and produce quinoline, the latter being also a coal-tar derivative, but up to the present time, in spite of the fact that quinoline is known as the skeleton of quinine, we have as yet been unable to produce the latter from quinoline.

CHAPTER I

TAR

Tar is a thick, dark-brown, viscid, oily liquid, produced during the dry distillation of coal; its chemical nature is very complex, and it contains a large number of compounds. The crude gas leaving the retorts is a mixture of permanent gases, but this mixture carries with it quite a number of hydro-carbon and other vapors, and as the illuminating, as well as the calorific, quality of coal gas is, in a great measure, dependent upon its hydro-carbon constituents, it is of prime importance to so treat the gas as to retain as many of these hydro-carbons as is possible. A reduction in temperature, however, soon reduces the hydro-carbons of greater density to liquid form, and this liquid is usually termed "tar." In spite of the fact that the gas temperature at the hydraulic main outlet is perhaps never lower than 145° F., large quantities of tar are deposited at this point, and it is, therefore, almost impossible to retain the hydro-carbons of this class in the gas with the usual method of condensation.

Both the nature of the coal used and the temperature of carbonization exercise a great influence upon the quantity, as well as upon the quality of the tar produced; thus both quantity and quality regulate the amount of revenue received, and in this manner govern to a great extent the final cost of gas production.

It appears from experiments conducted by Dr. Bunte, and afterwards confirmed by later experiments made by the Paris Gas Company, that the quantity of tar produced varies with the percentage of oxygen contained in the coal, the net results of these experiments leading to the statement that the greater the amount of oxygen present in the coal, the greater will be the amount of tar produced, this statement seeming also to hold good for ammonia production; on the other hand, it is stated that the greater the percentage of oxygen present, the less will be the production of coke.

Tar produced by high temperature carbonization contains but traces of paraffines and small quantities of olefines, but the acetylenes, benzenes, hydro-carbons, and naphthalene are present in large quantities, while the nitrogen is usually found in pyridine bases, and carbolic acid and cresols are the principal phenols; this tar also contains quite a quantity of what is known as "free carbon." Tar produced in vertical retorts contains paraffinoids in large measure, and its "free carbon" content, as well as that in coke-oven tar, is low, in spite of the fact that high carbonization temperatures prevail here; the cause of this difference in the quality of the tar is probably due to the travel of the gas, and which travel is influenced principally by the shape of the carbonizing chamber. "Mass" carbonization, as practiced in verticals and coke-ovens, as a rule produces better tar than "layer" carbonization as practiced in the older types of carbonizing apparatus, particularly where light charges are in use.

The term "free carbon" applied to this usual constituent of coal-gas tar is not exactly correct, as this constituent is not really a pure carbon, but a composition containing several other substances as well as volatile matter; experiments in a number of cases showed that after being precipitated, washed, and dried it usually appeared as a brown-black powder yielding about 8.5 per cent soluble matter of an oily, rather heavy nature, while the remaining ash contained quite an amount of oxide of iron. Against this we find, according to Allen, Vol. II, part II, page 55, that Behrens found "free" carbon to consist of 91 to 92 per cent of carbon, 3.1 per cent of hydrogen, and 0.4 to 0.9 per cent of ash.

As opposed to high temperature carbonization, the tars produced by low carbonization temperatures usually possess less naphthalene and hydro-carbons of the benzene series, but a larger proportion of paraffines and olefines, while the nitrogen usually appears as anilines.

The result of experiments conducted by L. T. Wright on the effect of temperature of carbonization as related to tar yield is shown in Table I, the temperatures of carbonization varying between 1112° F. and 1472° F.

The quality of tar produced also seems somewhat dependent upon the type of retort used, and very extensive tests were

made by R. O. Wyne-Roberts on this premise, the results of these tests being given in Table II, carbonization having been

TABLE I. — TAR YIELDS

Experiment number	1	2	3	4	5
Cu. ft. of gas per ton of coal	6600	7200	8000	10,102	11,700
Specific gravity of tar	1.086	1.102	1.140	1.154	1.206
Composition of tar (by per cent of weight)	%	%			%
Ammoniacal liquor	1.20	1.03	1.04	1.05	0.383
Crude naphtha	9.17	9.65	3.73	3.45	0.995
Light oils	10.50	7.46	4.47	2.59	0.567
Creosote oils	26.45	25.83	27.29	27.33	19.440
Anthracene oils	20.32	15.57	18.13	18.77	12.28
Pitch	28.89	36.80	41.80	47.67	64.08

carried out in horizontal retorts, vertical retorts, inclined retorts, and chamber ovens.

TABLE II. — COMPOSITION OF TARS

Composition	Horizontal retorts				Vertical retorts				Inclines	Chamber
	1	2	3	4	5	6	7	8	9	10
Specific gravity at 60° F.	1.20	1.25	1.22	1.25	1.10	1.12	1.119	1.13	1.095	1.18
Composition by distillation	%	%	%	%	%	%	%	%	%	%
Light oils, below 338° F.	3.10	1.10	1.40	1.10	5.85	1.70	3.70	2.30	4.40	0.40
Middle oils, 338 to 518° F.	7.68	13.10	10.50	13.10	12.32	21.90	20.20	16.50	28.50	10.20
Heavy oils, 518 to 662° F.	10.15	13.20	16.14	13.20	11.95	21.60	23.10	20.80	19.20	30.10
Anthracene	11.64	..	..	..	15.96	..	..	..	..	..
Pitch	62.00	72.60	71.80	72.10	49.75	54.80	52.60	60.00	47.50	53.90
Naphthalene	..	..	..	9.00	..	3.60	4.80	3.60	..	4.70
Free carbon	20.00	..	..	28.70	2 to 4	0.40	4.20	0.60	2.60	11.10
Water in tar	..	..	6.00	..	..	..	..	..	2.20	10.10

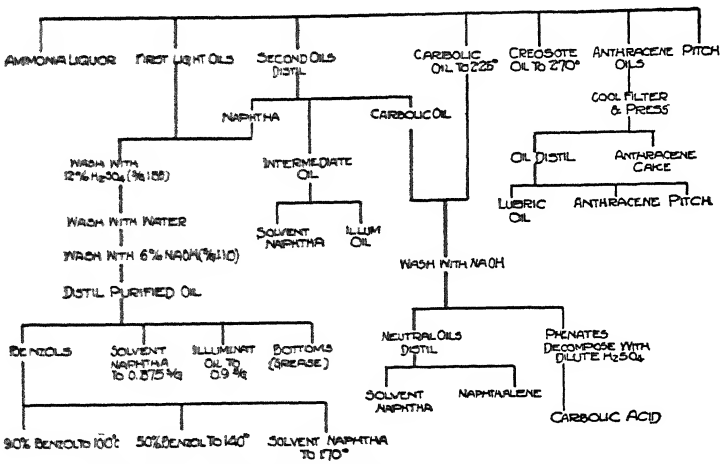


Diagram I. — Scheme showing the Refining of Fractions.

The distillation, or refining of coal-gas tar, is usually carried out to the fractions shown in Table III, while Diagram I shows the products secured by refining these fractions.

TABLE III. — TAR DISTILLATION

No. 1		No. 2		No. 3	
Fractions	Temperature C. degrees	Fractions	Temperature C. degrees	Fractions	Temperature C. degrees
Crude naphtha, or light oils ..	0 to 170°	First runnings, or first light oils	0 to 110°	Light naphtha	0 to 110°
				Light oils	110 to 170°
Heavy oils, dead oils, or creosote oils	170 to 270°	Second light oils	110 to 210°	Carbolic oils .	170 to 225°
		Carbolic oils .	210 to 240°	Creosote oils .	225 to 270°
Anthracene oils.	about 270°	Creosote oils..	240 to 270°	Anthracene oils	about 270°
Pitch	....	Anthracene oils	about 270°	Pitch	....
		Pitch			

The Removal of Tar. — In the usual systems as applied at present, the removal, or the precipitation, of tar is accomplished by condensation or cooling; quite an amount of condensation occurs between the retort and the hydraulic

main, a further amount of tar being deposited in the hydraulic main proper, after which the gas is conducted to the condensers, where gradual cooling further reduces the tar content. After leaving the condensers the gas still contains quite a number of tar globules in suspension, the removal of these last traces of tar being only possible by means of friction, a Pelouze and Audouin condenser being the usual apparatus employed for this purpose.

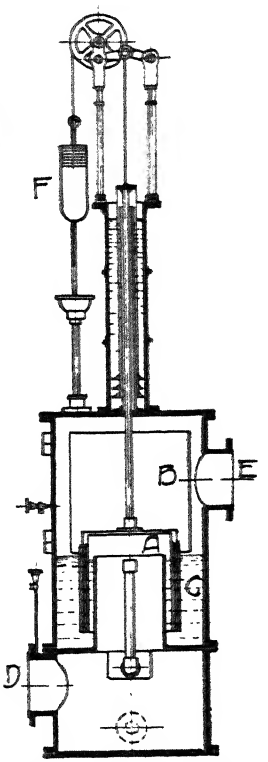


Fig. 1.— Pelouze and Audouin Condenser.

This condenser is subject to quite a variety of forms, but the construction of the various types all depend upon the same principle (see Fig. 1). In this machine a friction bell (*A*) is suspended in a cylindrical casing (*B*), the bell dipping into a reservoir (*C*) containing ammoniacal liquor. This bell consists of several sections arranged in pairs concentrically, the inner section of each pair being perforated with small round holes facing a blank space on the next outer section, the perforations in this outer section being somewhat larger than those of the inner. The gas enters at (*D*) and passes up and under the friction drum, or bell, finding emission from the latter through the holes in the various shells or sections; the tarry vapors are "wire-drawn" and condensed in passing through the perforations, striking against the blank space opposite the holes and being thus deposited on the shell of the drum, flowing to the bottom and thence to the overflow, the gas passing on and out at (*E*). The friction drum is suspended and so balanced as to act as its own regulator, the drum rising or falling in the hydraulic seal as the make of gas increases or diminishes, the amount of seal for maximum make being regulated by the counterweight (*F*), thus causing a larger or smaller number of openings to be exposed to the passage of gas.

Another type of tar extractor is built in the form of an injector Fig. 2., and is used in connection with the Otto by-product coke-oven system; here the gas is sprayed with a stream of tar as it enters the apparatus at (*A*), the tar being collected in a drum and a certain portion being continuously pumped back to the spray by means of a rotary pump. The gas leaves the drum through a series of perforations in the outlet pipe.

The Simon-Carves Company uses what is known as a cyclone tar extractor, the shell or body of which is cylin-

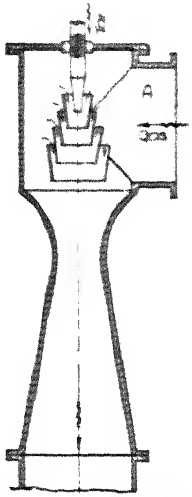


Fig. 2.—Injector Type of Tar Extractor.

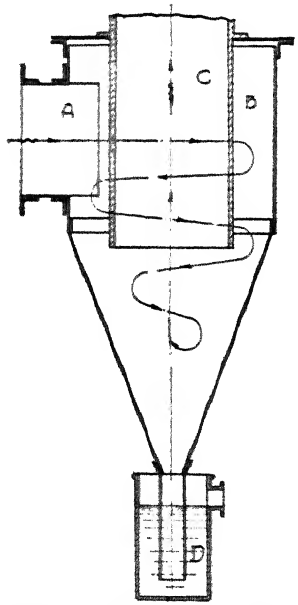


Fig. 3.—Cyclone Type of Tar Extractor.

drical at the top and ending in a deep cone at the bottom. The gas enters at (*A*) and is whirled around in the body of the machine (*B*), leaving through the central pipe (*C*); the condensed tar leaves at the bottom of the apparatus and enters a seal at (*D*) (see Fig. 3).

The centrifugal tar extractor is built up of a fan casing containing a series of blades mounted upon a rapidly revolv-

ing shaft; the gas enters the casing at (A), Fig. 4, and is whirled about through the medium of the fan blades, the heavier tar particles being hurled out against the casing by centrifugal force. The rotary tar extractor (Fig. 5) is built up of a cylindrical, drum-like shell, a horizontal shaft passing through its center; a perforated drum is mounted on the shaft, and a second perforated drum, inclosing and concentrically surrounding the former, is mounted on a hollow spindle, the two drums revolving in opposite directions through the medium of a set of planetary gears. The per-

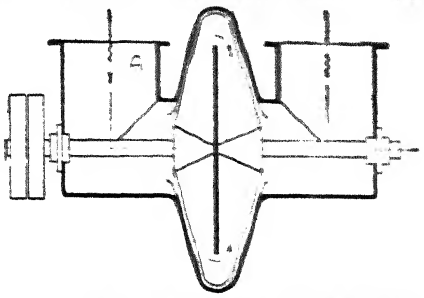


Fig. 4.— Centrifugal Type of Tar Extractor.

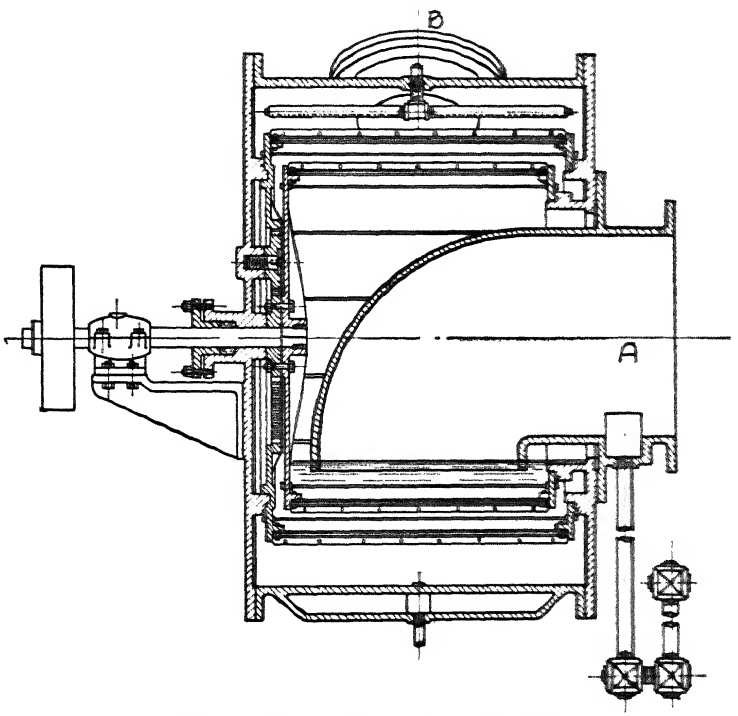


Fig. 5.— Rotary Type of Tar Extractor.

forated drums are built in sections, the flanges connecting the sections forming a portion of a helix, so arranged that as the drums revolve in the liquid tar kept in the bottom of the casing, they are caused to pick up tar and spread it over the revolving drums thus causing the gas to pass through a thin film of tar in finding egress from the interior of the drums. The bottom of the casing is provided with a steam pocket for the purpose of heating the deposited

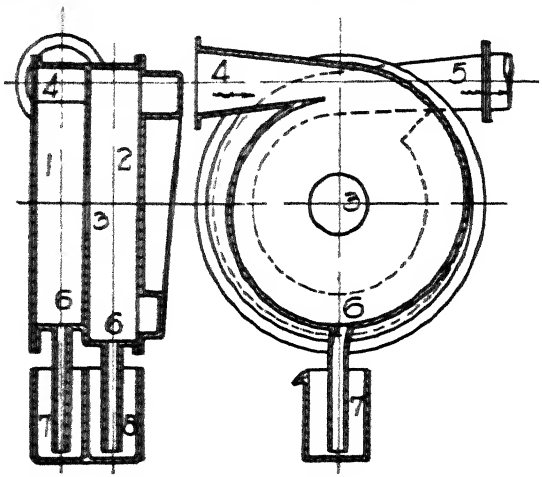


Fig. 6. — Centrifugal Type of Static Tar Extractor.

tar if this should be found necessary. The gas enters the machine at (*A*) and leaves at (*B*).

Another centrifugal tar extractor, without moving parts, is shown in Fig. 6, and it consists of two compartments marked (1) and (2) which communicate with each other through the central orifice (3). The gas enters the device at (4) and is then thrown tangentially against the periphery of the first compartment (1), centrifugal motion being imparted to the gas by the circular shape of the casing, this centrifugal or swirling motion increasing in rapidity as the gas approaches the central orifice (3), thence passing into the second chamber (2), where centrifugal motion is again imparted to the gas, but in an expanding ratio instead of a contracting one, as is the case in compartment (1).

M. J. Mazeron (see "Gas World" June 27 1914) states that the centrifugal force in both the contracting and expanding swirl varies inversely as the cube of the radius of the gas path, thus attaining high values. The entering gas is projected against the tar already deposited on the periphery of the inlet compartment (1), while in compartment 2 the action is reversed, thus causing the tangential velocity to decrease as the gas travels towards the periphery of compartment (2), the pressure being thus restored. The gas leaves the extractor at (5), while the deposited tar flows out at (6) into the seal pots (7) and (8). Mazeron also states that from the point of view of tar separation, compartment 2 is of greater importance than compartment 1 but that the latter chamber has the effect of making the tar vesicles coalesce.

The speed of the gas just before it passes through the central orifice (3) is said to be about 500 feet per second and the pressure absorbed by the device is about 2.4 inches of water.

The tar, after its removal from the gas, usually contains quite an amount of ammoniacal liquor, from which it is separated in a separating well, the ammonia passing off on one side to storage, and the tar on the other. In order to separate the tar from any liquor or water which may still remain in combination, the tar may be worked up in a centrifugal dehydrating plant, shown in Fig. 7. The tar is cleared of water and heavy particles in this machine and is thus purified. The tar is heated to from 85° to 95° F. in the heater (*A*); after which it passes through a filter (*B*), and thence by means of a special valve into the drum of the centrifugal, the latter making about 2500 revolutions per minute. The heavier tar is thrown out by centrifugal force against the shell of the machine and rises up the sides to the top of the disc (*C*), where pipe (*D*) takes up the tar and pipe (*E*) the liquor, this liquor being returned to the ammonia well. All of the heavier particles in the tar, such as coke dust and other substances which are insoluble in benzol, are collected in the lower portion of the drum and can readily be removed when the drum is being cleaned, it being necessary to clean the drum every six to twelve hours, depending upon the condition of the tar.

At one plant where these centrifugals are in use, the separation of liquor from tar has produced an increased revenue of $5.75 per day with the daily treatment of 2800 gallons of tar, producing 2452 gallons of liquor free tar, selling at 17.5 per cent more than the former price, and separating 448 gallons of ammonia liquor which is sold independently of the tar, this additional net revenue being secured after deducting

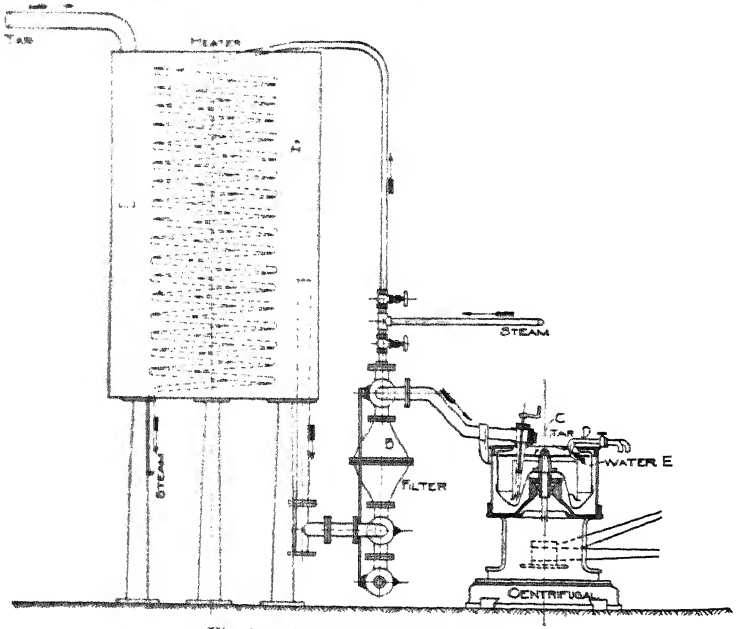


Fig. 7.—Tar Dehydrating Plant.

labor, operating cost, and interest and amortization on the capital expended.

All of these methods for the removal of tar, with the exception of the Otto system, are dependent upon cooling or condensing the gas, and the final product, including that of Otto, must later be distilled in order to secure its various constituents.

Opposed to this system is the one devised by Feld, in which the heat contained in the gas is utilized by a system of fractional coolings to separate, or wash out of the gas, tar in several of its principal constituents. This treatment may

also be varied in such manner as to prevent the formation of tar as much as possible by maintaining the heat of the gas coming from the retorts at a temperature above the dew point of the gas for the constituents of high boiling points. This may be done by covering the connections from the retorts to the first washer with insulating material, or by applying heat to the exterior of the pipes. The gas thus protected is led to the washers, where it is subjected to fractional cooling and successive washings at successively lower temperatures, so that the various tar constituents are separated from each other by employing the temperature of the gas itself, and without the necessity of employing extraneous heat after previous cooling.

The Feld System of Fractional Separation of Tar Products. — As no tar separating plants of the Feld system have as yet been erected in the United States, statements showing results obtained in this branch of by-product recovery will necessarily have to be confined to European practice.

In Europe we find that the distillation of 1000 kilos (2200 pounds) of coal produces on an average

30 kilos (66 pounds) of tar,
120 kilos (264 pounds) of water, and
300 cbm. (10,590 cu. ft.) of gas,

measured dry at 0° C. and 760 mm. pressure, and that this average will give

100 grammes of tar, and
400 grammes of water per cubic meter of gas.

The dew point of this gas for water lies between 70° and 75° C. (158° and 167° F.), or, to be more explicit, at 72° C. (162° F.), which means that the gas can be cooled to several degrees above 72° C. without condensing the water vapors.

As stated before, tar is a mixture containing more or less so-called free carbon, with hydro-carbons and other organic substances of various boiling points, generally designated by Feld as follows:

Light Oils, with a boiling point up to 170° C. = 338° F.

Creosote Oils, with a boiling point from 170° to 230° C. = 338° to 446° F (also termed medium oils).

Heavy oils, with a boiling point from 230° to 270° C. = 446° to 518° F.

Anthracene Oils, with a boiling point from 270° to 320° C. = 518° to 608° F., while the residue after distillation, consisting of from 20 to 30 per cent of free carbon and hydrocarbons, with a boiling point above 320° C. (608° F.), is known as pitch.

The products due to tar distillation are of a secondary nature, that is, they are produced by means of a second more or less disintegrating process of distillation, and their condition and respective volumes are not at all identical with the primary tar ingredients contained in the gas. This statement seems to be borne out by the fact that soft pitch produced from the gas by Feld's process only contains from 1 to 3 per cent of "free carbon," while the usual pitch produced by distillation contains at times from 20 to 30 per cent of "free carbon."

Due to the fact that these products are produced by such secondary distillation, it becomes almost impossible to determine by computation how much of these primary constituents were contained in the gas based upon the amount of oils and pitch produced during the distillation of the tar.

Just as in the case of water vapors, the vapors of tar constituents, which are capable of vaporization at variable temperatures, produce variable tensions, and this vapor tension increases the closer the temperature approaches the boiling point of the liquid in question. According to this vapor tension, the gas, coming in contact with one of these fluids, will absorb a certain portion of the fluid in vapor form at a certain temperature, or the gas will saturate itself with the vapor of the fluid in question. The amount necessary for saturation increases with the temperature of the gas, and therefore has a fixed relation to the latter.

If, on the other hand, a gas having a temperature of B°, saturated with the vapors of any fluid, be heated to a higher temperature of C°, without remaining in contact with the vapor producing fluid, the gas will at the temperature C, or at any other temperature above B, no longer saturate itself with the vapors of the fluid, and the gas will then be superheated with reference to the vapors of the fluid in question.

If we bring this gas, or a gas of a hydro-carbon character, in a superheated condition into intimate contact with hydro-carbons, it will, just as in the above case of saturation, evaporate hydro-carbons and the gas will saturate itself with the product of this vaporization. The vaporization will be complete in proportion to the heat content due to superheating, and there will also be a decrease in volume as well as in temperature.

This reduction in temperature is not, however, always accompanied by cooling, or by the extraction of heat, as the heat content existing before superheating has been converted into latent heat in the vapors of the hydro-carbon. Only when the fluid to be vaporized is much cooler than the caloric compensating point (see "Cleaning of Blast Furnace Gas," McGraw-Hill Book Co., Inc., New York), and when the mass of the fluid is very large, the heating of the mass which cannot be brought to the point of vaporization will absorb heat and produce a corresponding cooling of the gas. By regulating the mass and the temperature of the fluid to be evaporated it becomes possible to permit or avoid a reduction in the heat contents of the gas.

The following will explain what Feld terms the "caloric compensating point." The heating of water saturated gas at and from 40° C. to 250° C., without the additional absorption of water vapor, or the superheating of a gas saturated at 40° C. to a temperature of 250° C., causes the heat content to increase from 51.7 calories by 75.6 calories, giving a total of 127.3 calories, or just as much additional heat as if the gas had been heated from 40° to 58° C. with the simultaneous absorption of water vapor. This higher temperature, or 58° C. in the above example, is the "caloric compensating point" for a gas superheated to 250° C. and whose dew point for water is at 40° C.

The changes in condition are therefore, in the case of saturation with the vapors of tar constituents, considerably less than would be the case if the gas had been saturated with water vapors; the heat of vaporization of the hydro-carbons under consideration is about one-seventh that of water vapor. For example, if the heat of vaporization of benzol is 92.9 calories, of toluol 83.6 calories, of xylol 78.3

calories, the heat of vaporization of such tar constituents as have a higher boiling point will be still less.

If the superheated gas is simultaneously mixed with several hydro-carbons, or with such as will permit of mixing or of being absorbed, the one with the lower boiling point will also act as a gas and saturate itself with the vapors of the one having the higher boiling point; but the conditions governing a case such as this are not so readily explained as if we were dealing with water vapors, or with the vapors of non-mixing fluids. In the case of mixing fluids the tension of vaporization changes for the various constituents, and the final results, which of course are of the most importance, due to the mixing qualities of the hydro-carbons with the constituents of low boiling points, will cause the vaporization of a greater mass of the fluids of higher boiling points than would be the case if the latter fluids were present in an unmixed condition.

In accordance with the heat contents corresponding to the degree of superheat of the gas, and to the mass of constituents of low boiling points active in the gas, the gas will wholly or only partially saturate itself with the vapors of the fluids in question; it is therefore possible that the gas may saturate itself with the vapors of the high boiling constituents (as their tension of saturation is lower), but will remain superheated with reference to the low boiling constituents.

If, for example, the superheated gas should be cooled by means of outside coolers, a portion of the high boiling constituents with which the gas had saturated itself, will immediately condense, and the amount of condensation will be proportional to the decrease in temperature; but the lower boiling constituent can only separate itself after the gas has been cooled to the temperature corresponding to the dew point of the fluid in question.

In this case we also find the conditions which govern the mixable fluids altered, as the dew point of the lower boiling constituents rises if at the same time a high boiling constituent, which will mix with the lower one, is separated from the gas.

Coal gas and similar gases are in this unsaturated condition with reference to the oily tar constituents contained in the

gas when it leaves the retort, but it will be saturated with the major portion of the bitumen constituents. The dew points of this gas for these various constituents lie at varying lower temperatures, and are dependent upon the boiling points and the masses of the various constituents of the gas.

Feld determined that the dew points of the usual coal gas for the greater portion of the bitumen tar constituents lie above 200° C. (392° F.), and for the greater portion of the oil constituents below 200° C. As long as the gases are not cooled below 200° C., only unimportant quantities of the oily tar constituents will be separated: of course, this temperature of extraction varies in accordance with the quality of the coal used and of the gas produced.

In order, then, to extract the tar constituents directly and fractionally from the gas, and which has heretofore only been accomplished by secondary distillation of the tar, Feld proceeds as follows:

The gases coming from the benches or the coke-ovens, as the case may be, are protected against condensation by wholly or partially insulating the hydraulic main and pipe connections, so that the temperature of the gas does not drop below the point at which tar products of low boiling points are separated. For the removal of the other tar products, Feld employs his centrifugal washer; in these washers progressive cooling, or progressive cooling combined with progressive washing, is attained through a progressive drop in temperature, and in this manner various tar products are obtained and separated from each other through the medium of the heat of the gas itself.

This treatment of the gas can be employed to secure any number of tar constituents; in case it is desired to secure pitch and tar oils of higher boiling points, two washers are employed, and they are operated in such manner that the temperature in the second washer remains above the dew point of the gas for water; or, for example, if it is not desired to separate pitch from the other constituents, those constituents of the tar which have higher boiling points can be separated from the gas in one washer by maintaining a temperature near the dew point of the gas for water.

Cooling down to the desired temperature can be wholly or

in part accomplished in surface coolers, but it is of prime importance and advantage to cool the gas to a given separation point by washing the gas with a liquor produced from the products secured during a later period of separation, or with liquids which contain tar constituents with which the gas cannot saturate itself at the given temperature.

The drop in temperature of the gas is thus produced by the vaporization of the tar constituents in question. Generally speaking the gases are cooled at one point of progressive separation by washing them with the fluids of a later period of progressive separation; it is therefore immaterial whether the washing liquids are taken from the gas itself, or whether they are secured from outside sources. In the following description the separation of pitch is included, and it is assumed that the pitch, or bitumen-characterized constituents, shall not contain any products with a boiling point below 320° to 350° C. (608° to 662° F.).

The gases are cooled down to the dew point of such constituents as have a boiling point of from 320° to 350° C. either in the first washer, or just before entering the washer. As is well known, the dew point for the greater number of constituents lies above 140° to 160° C. (248° to 320° F.); within these temperatures such constituents as have boiling points of 320° C. and above are extracted, or such constituents with which the gas will not saturate itself at from 140° to 160° C.

The constituents extracted at the given temperature leave the washer as a hot fluid which congeals upon being cooled to about 70° C. (158° F.), depending upon its content of hydrocarbons.

The gases coming from the first washer are thus practically freed of carbon and pitchy tar constituents, and they contain principally tar oils with boiling points below 350° C. (662° F.); in addition to this, the gases contain such portions of the constituents having boiling points at and above 350° C. as are equivalent to the vapor tensions of the constituents corresponding to a temperature of 160° C. (320° F.), while the vapor tension of the bitumen tar constituents is very low.

Those tar constituents which have a dew point from 160° C. down to that for water, in this case above 75° C.,

are removed from the gas in the second washer, assuming that the dew point of the gas for water is at 72° C.: the gas is consequently cooled down from 160° to 75° C. The lowest boiling point of any product separated during this drop in temperature is, for example, at 250° C. (482° F.), and in addition to constituents with boiling points of from 250° to 350° C. the product will contain such an amount of constituents with boiling points above 350° C. as will be equivalent to the reduction in vapor tension of the gas for these constituents.

In order to separate as far as possible those constituents having boiling points above 350° C. from those of lower boiling points, as much of the separated product coming from the second washer is pumped into the first washer as is required to reduce the temperature in the first washer down to 140° to 160° C. (284° to 320° F.). Upon the entrance of this liquid into the first washer, the constituents with boiling points below 350° C. (662° F.) vaporize, because the gases at 160° C. and above are not saturated with them. Those constituents with boiling points above 350° C. with which the gases are saturated at 160° C. cannot vaporize.

This method of operation is best employed in cooling the gas and at the same time causing the greatest possible separation of the various tar constituents from each other; thus the greatest possible number of constituents with boiling points at and above 350° C. are separated in the first washer, while the separated product from the second washer will experience a reduction in contents of such products as have boiling points at and above 350° C.

In some cases Feld advises the insulation of the washer proper, in order to prevent chilling the outer surface of the gas, and also in order to be in a position to pump as great a quantity of the product coming from the second washer into the first one as is possible.

Instead of using the tar products which have been taken from the gas for cooling and washing, it is possible to use tar taken from other sources, which tar is thereby separated into its constituents and later recovered in its separated state during the process of cooling and washing. It is well to note here that this tar, which is thus distilled through

the agency of the heat of the gas itself, does not take up any free carbon because the distillation is accomplished at very low temperatures.

Instead of fractionately separating the tar constituents of high boiling points as described above, the constituents can be jointly washed out at a temperature slightly above the dew-point temperature of the gas, in this case from 72° to 80° C. (162° to 176° F.), but in both cases the gas leaving the last, or heavy oil washer as explained above, or upon leaving the hot tar washer described below, will be free of tar and at the same time retain a temperature above the dew point for water. As far back as 1903 Feld freed the gas of tar by hot tar washing before a temperature equivalent to the dew point for water was reached.

A Feld washer especially arranged for hot tar washing is shown in Fig. 8, and in order that condensation may be avoided in the washer by reducing the temperature of the gas to the dew point for water, the washing tar should be heated to from 40° to 60° F. above the temperature of the gas at the inlet to the washer, this hot tar being the active tar-extracting medium.

Referring to Fig. 8, which shows a portion of a Feld washer with superimposed Pelouze condenser,

A = Pelouze condenser,
B = Gas port in washing chamber,
C = Upper washing chamber,
D = Lower washing chamber,
E = Gas inlet,
k = Basin, or tank containing wash tar,
r = Radiator, or steam coil,
l = Rotary tar pump,
m = Preheater for wash tar,
s = Insulated connection from tank (*k*) to pump (*l*).

In order to keep the wash tar at the desired temperature, the steam pipe from (*m*) is located beneath the pipe (*s*).

The hot wash tar is pumped from tank (*k*) through the insulated connection (*s*) and preheater (*m*) to the Pelouze condenser (*A*) through the overflow pot (*n*); any surplus tar overflows at (*o*) and (*p*) and returns to tank (*k*).

The tar overflows from the Pelouze through (*b*) and (*d*), (*e*) and (*g*) into the upper chamber (*C*) of the washer, where

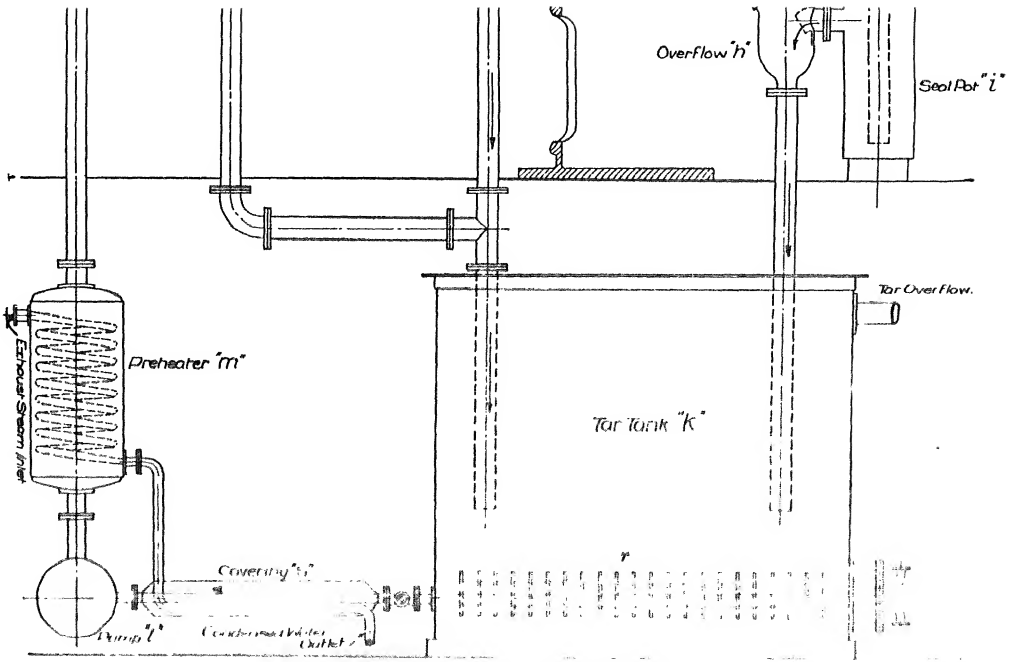


FIG. 8. -FELD HOT TAR WASHER

(Facing Page 24)

it is picked up by the washing cones within the chamber and spread out over the entire gas space, the depth of the spray being from 8″ to 14″, depending upon the size of the washer. The gas is thus brought into intimate contact with the hot wash tar and is subjected to a thorough washing, the wash tar, as well as the tar expelled from the gas, overflowing through the gas port to the next lower washing chamber; here the wash tar is again placed in circulation by the cones in this chamber, and the total combined tar finally leaves the washer through the pot (*i*) attached to the gas inlet connection, and by means of overflow (*h*) enters tank (*k*), all surplus tar from this tank flowing off to the tar storage.

In order that the maximum results may be secured, the wash tar should be constantly circulated through the washer, but it is not always necessary to circulate it through the Pelouze condenser, this omission being dependent upon the condition of the tar in the gas. The amount of hot tar to be circulated through the washer may vary from 0.5 to 2.5 gallons per 1000 cubic feet of gas per hour; larger volumes of gas require less circulating tar than do smaller volumes, but the amount of washing tar circulated must be so regulated as to prevent the temperature of the gas reducing the temperature of the wash tar.

The circulating wash tar should be pumped through the preheater (*m*) before it enters the washer, this preheater being supplied with a steam coil, and in some cases it may be necessary to insulate the tank containing the wash tar, depending upon its location, and even the washer proper with some insulating material in order to increase the efficiency, as many of these washers are set up in the open in Europe, being thus exposed to the weather.

The tank containing the wash tar is also provided with a steam coil, or radiator, made in one piece in order to prevent leaks and thus mix water with the tar. Care must be exercised in operation to the extent of preventing a deposit of thick tar in the Pelouze condenser, and if the washer should be stopped for any reason it must be emptied of tar at once in order to avoid cooling the tar and thus clogging up the passages.

TABLE IV.—FILLED HOT TAR WASHING

Washer without Pelouze Condenser

Date and number of test	Tar vapors in grains per cubic foot		Grains removed	Efficiency	Gas passed per 24 hours cubic feet
	Inlet	Outlet			
[illegible]	[illegible]	0.2650	11.219	97.46	2,463,000
[illegible]	[illegible]	0.2160	10.170	97.92	2,453,832
[illegible]	[illegible]	0.2930	10.525	97.29	2,341,800
[illegible]	[illegible]	0.4170	13.101	96.92	2,397,000
[illegible]	[illegible]	0.5250	9.382	94.70	2,400,000

Washer with Pelouze Condenser

[illegible]	[illegible]	0.0436	10.0064	99.56	2,600,000
[illegible]	[illegible]	0.0872	13.0128	99.34	2,600,000

Table IV gives the results secured in washing with hot tar, the washer being supplied with a Pelouze condenser in the one instance but not in the other.

This method of operation has made it possible to extract ammonia, hydrogen-sulphide, and cyanogen by chemical washing at high temperatures, and which would not be possible if the gas contained tar; this high temperature washing not only prevents the production of weak solutions of these valuable gas constituents, but it also prevents losses to a great extent. The tar-free gas, at a temperature with which it leaves the washer, is subjected to further washing in a series of centrifugal washers, and as explained in the following pages, where the ammonia, cyanogen, and, if the plant is so arranged, also hydrogen sulphide, is removed.

After leaving the last ammonia washer the gas still retains a temperature close to that of its dew point for water, and is therefore still saturated with water vapors; besides this, the gas also carries the vapors of those tar constituents which have boiling points of 250° C. and above, these having been separated from the tar in the washers preceding those for ammonia, etc.

This gas also contains all tar constituents having boiling points below 250° C., that is, middle oils, naphthalene, light oils, xylol, toluol, and benzol. In order to expel these middle oils, that is fractional distillation at boiling points down to 200° C., the gas is so far cooled as to retain a temperature still somewhat higher than the dew point for light oils, which latter have their boiling points at and below 200° C. According to Feld, after having been subjected to hot tar washing, coal gas can be cooled down to 18° C. (65° F.) without expelling any appreciable quantity of light oils.

This cooling down from 72° to 18° C. can now, as the gas no longer contains any valuable constituents which are soluble in water, be performed in an additional centrifugal washer by bringing the gas into direct contact with water. With the middle oils a volume of water, corresponding to the drop in temperature, is also expelled, or in the case described above, 400 — 15 = 385 grammes of water per cubic meter of gas.

This water readily separates from the oil expelled with it, and this oil contains nearly all of the naphthalene emulsified in water; after the water has been separated from the mixture the naphthalene can be directly removed. If the expulsion of naphthalene by cooling down to 18° C. should be so great as to cause stoppages, the cooling should be performed in two fractions; first, the gas should be cooled to slightly below the dew point for naphthalene, 25° to 35° C. (77° to 95° F.), and then the naphthalene washed out of the gas by employing the middle oils expelled in the preceding washer as a washing medium.

After complete cooling the gas now still contains all of the light oils, especially the low boiling hydro-carbons like benzol and its homologues, and with which the gas has not saturated itself, that is, their partial tension in the gas is lower than the vapor tension of those constituents at the lowest temperature to which the gas has been cooled.

A gas thus treated, and one which is to be used for illuminating purposes, possesses a higher illuminating power than if it had been condensed and purified in the usual manner, or by the common method of condensation with the common expulsion of the various constituents.

In the present practice, due to common separation and

vaporize the constituents of high boiling points act as solvents for those of lower boiling points, but, as is well known, the vapor tension of a solution is always lower than the vapor tension of the pure constituent, and therefore, in accordance with the old practice of purification, low boiling tar constituents, such as benzol, are to a greater or less extent expelled from the gas, thus reducing its illuminating power in direct proportion to the amount thus removed.

These low boiling constituents, which are so valuable to the illuminating quality of the gas, will, due to the present method of condensation, pass off or be expelled in part with the tar, from which they must be regained by separate distillation, while in the cold process of condensation they remain in the gas.

If it should be desired to also expel these constituents from the gas, the latter should be washed after final cooling with tar oils of high boiling points, and which were expelled from the gas at a previous period of the process. Such high boiling tar oils have, at the low temperature in question, a very low tension, and as this tar oil was taken from the gas itself the gas is already saturated with these oils in an amount equivalent to the low vapor tension. In consequence, due to the use of these high boiling tar oils for washing purposes, or for removing benzol and its homologues from the gas, the gas will not absorb any of the oil, but on the contrary, as the gas suffers a reduction in volume when the benzol is expelled, a very small volume of this wash oil is also expelled, together with other high boiling tar constituents from the gas, and the latter is thereby made cleaner.

The light oils can now be distilled from the products having high boiling points, and which were used for washing out the light oils, after which they are again returned to the washers as washing media; as soon as this wash oil has saturated itself with impurities, and thus becomes valueless for benzol washing, the impure oils of high boiling points are used for washing in a preceding stage, for instance in the first or second washer for cooling and washing purposes, where the low boiling constituents are vaporized and then recovered in their original and pure condition further on in the process, while the constituents of higher boiling points

remain in the product coming from the washer in question.

Feld's process for the separation of tar from gas has been in operation at various European plants since 1906, originally as an experiment but finally as a permanent method of operation. Below are given several operating results secured in practice.

At a coke-oven plant in Upper Silesia the gases produced by the carbonization of 395 tons of coal per 24 hours were treated in two Feld washers operated in parallel, the temperature of the gas averaging 150° C. (302° F.) with the following results:

Temperature of gas, 150° to 160° C. = 302° to 320° F.

Temperature of pitch expelled from washer 150° C. = 302° F.

Product obtained, 5500 pounds of thin soft pitch.

Upon heating this pitch to 340° C. (644° F.) the following products were obtained:

	Test No. 1	Test No. 2
Oil and water at 315° C. (599° F.)	2.6%	7.0%
Residue after 340° C. (644° F.)	97.4%	93.0%

The Feld process was installed at a Bohemian "brown" coal works in 1907; here the gases pass through a number of Feld washers and surface coolers. The results given during a test run showed that due to the large percentage of water in the "brown" coal, the dew point of the gas was found to be between 90° and 92° C. (194° and 198° F.). The gases are brought from the ovens with a temperature of 110° C. (230° F.), and enter the first Feld washer at 89° C. (192° F.); owing to the large amount of condensed water, three Feld washers were used in series in order to wash out the separated bitumen and heavy oils, which, at 89° C., were present in the water in the shape of fog. The expelled products at various temperatures are given in Table V.

The constituents gained upon distilling these products are given in Table VI; columns 2, 3, and 4 give the quantities secured in a percentage of the whole distilled off at the temperatures given in column 1.

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TABLE V.—BROWN COAL PRODUCTS

Apparatus	Gas from generator Cubic ft.	Expelled product: Bitumen lbs.	Oil I, lbs.	Oil II, lbs.	Efficiency %
1st washer	89	1840			97.4
2d washer	89	132			2.5
3d washer	89	3.5			0.1
1st cooler	70.8		1.32	..	..
2d cooler	55			1320	..
Total in 24 hours		1884.5	1932	1320	..

TABLE VI.—PRODUCTS OF DISTILLATION

Appearance and condition	Bitumen	Oil I	Oil II	Oil III
	Hard resins at 30° C.	Light, running	fluid	Very light
Specific gravity	0.9607 at 35° C.	0.92 at 16° C.	0.896 at 16° C.	
Temperature of saturation	to 80° C.	From 98° to 76.8° C.	From 76.8 to 35° C.	From 78° to 20°

PRODUCTS OF DISTILLATION

	%	%	%
To 120° C.			0.2	9.0
" 140° C.		0.5	2.5	15.0
" 160° C.	1.0	1.5	6.0	40.0
" 180° C.	1.5	5.0	25.0	57.5
" 200° C.	1.8	24.5	58.5	87.0
" 220° C.	3.0	56.0	83.5	95.0
" 240° C.	10.5	78.5	94.5	..
" 255° C.	17.5	86.5	98.0	..
" 270° C.	26.0	92.5	..	..
" 285° C.	35.0	96.0	..	..
" 300° C.	43.5	.	..	..
" 320° C.	57.0	.	..	..
" 340° C.	66.0	.	..	..
" 360° C.	76.5	.	..	..
" 365° C.	80.0	..	..	..
Water	1.0	0.5	0.2	..
Residue of soft pitch	19.0	3.5	1.8	..

The last column of Table VI shows a light oil which was expelled or separated when the gases were cooled down from 78° to 20° C.

It should be noted here that before the introduction of the Feld process of fractional distillation in washers, the production of pitch by the usual system of condensation and distillation amounted to as much as 35 per cent, and after the introduction of this process the pitch production in the same works was as low as 7.5 to 12 per cent, the production of valuable oils increasing in the same ratio. The tar produced by the old process sold for $5 per ton, while, with the oils produced directly from the gas by Feld's system, the equivalent in oils and pitch sold for $16 per ton.

At the coke works of the Ilsider Huette, fractional distillation, by Feld's process, has been in operation for some time with the results given in Table VII.

TABLE VII. — ILSIDER RESULTS

Temperature of separation	Product No. 1 to 70° C.	Product No. II 70° to 30° C.
	Products of Distillation	
	%	%
To 135° C.	..	3.75
" 200° C.	1.1	10.75
" 230° C.	1.9	..
" 240° C.	2.4	37.75
" 250° C.	..	58.55
" 270° C.	12.4	68.95
" 300° C.	17.6	80.05
" 340° C.	24.3	..
Residue after distillation	75.7	19.95

Product No. I, Table VII, is absolutely free of naphthalene and only contains from 1 to 3 per cent of "free carbon"; according to reports received from the Huette this product is an excellent material for lining the steel converters, owing to its high percentage of bitumen. While the use of the tar ordinarily produced and containing from 20 to 30 per cent of "free carbon" only permitted of from 25 to 30 charges in the converter before relining became necessary, a lining of this new product permitted of 62 charges, all other

conditions remaining the same, and the life of the converter lining was thus increased by more than 100 per cent.

Product No. II is a middle oil from which the greater portion of the naphthalene can be pressed; after cooling the gases down to 18° C. the oil of product II is used to wash out the light oils and benzol.

The tar-washing plant erected by Feld at Moncieu, Belgium, is being operated with the results shown in Table VIII

TABLE VIII — MONCIEU RESULTS

Temperature of separation	Bituminous tar		Creosote oil
	Product I	Product II	Product III
Specific gravity			
I at 25° C.	1.175		.
II at 20° C		1.135	.
III at 17° C		.	0.96
Viscosity at 50° C. (H_2O at 50° = 1)	8.0	6.9	..
Carbon contents (Anyline, Pyridine, Methane)	0.23%	0.32%	..

PRODUCTS OF DISTILLATION

	%	%	%
To 140° C.		.	..
" 190° C. ..		.	10.0
" 200° C	.	.	29.5
" 210° C . .	..	..	47.5
" 220° C	.	..	66.0
" 230° C	..	.	81.5
" 240° C.	.	..	88.0
" 250° C. . . .	..	3.5	93.0
" 260° C ...	.	.	96.0
" 270° C . ..	2.0	9.5	..
" 290° C.	9.5	11.5	..
" 300° C.	11.5	13.0	..
" 310° C. . . .	13.0	16.5	..
" 320° C.	15.0	.	..
" 330° C. ...	..	18.5	..
" 350° C. . .	.	24.5	..
" 360° C. . .	36.5	45.5	..
Residue	60.0	45.3	40.0
Melting point of residue	53.5° C.	60.5° C.	..
Acid oils .	1.0%	2.9%	..
Bases	1.8	2.2	..

Another system of tar extraction, and one which has been used with success on producer gas, consists in cooling the gas to a degree sufficient to condense the tar vapors, after which the gas, together with the tar, is passed through a porous diaphragm of spun glass, placed between two metal screens. It is stated that in passing this diaphragm an important change occurs in the physical state of the tar. On the inlet side, the tar exists as a large number of minute particles ordinarily known as tar fog, and in passing the diaphragm these particles coalesce, so that on the discharge side the tar particles are of relatively large dimensions which cannot be carried along with the gas current and they immediately separate out by gravity.

This extractor is shown in Fig. 9; after the gas has been cooled, it is delivered under pressure by means of the pump (*B*) into the main (*C*), then passing through the diaphragm (*E*) and discharged from there into the main (*F*), while the tar accumulates in the separator (*G*), from whence it is withdrawn to storage.

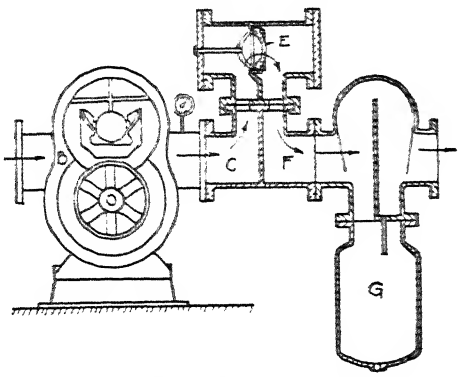


Fig. 9.—Static Type of Tar Extractor.

In the electrical precipitation of tar the duty of the electric field is to agglomerate the fine tar particles so that they can readily be removed later in some form of mechanical separator, and it is stated that this agglomeration can proceed without regard to temperature, thus retaining the light oils in the gas and increasing the illuminating power. This latter system closely approaches the results secured with that of Feld in that tar can be removed at a temperature above that of the dew point of the gas for water, but the Feld is the only system which can secure these results with a simultaneous separation of the tar into several of its fractions.

Experiments covering the electrical separation of tar from coal gas have been under way for some time, and the principal

difficulty to be surmounted seemed to lie in the selection and design of the electrodes.

In a report made to the Michigan Gas Association by Prof. A. H. White, R. B. Rowley and C. K. Wirth, on the experiments conducted at the plant of the Ann Arbor Gas Company, Ann Arbor, Mich., it is stated that the tar separator consisted of a six-inch gas pipe, felt-jacketed, about six feet long, set vertically; the gas was conducted into the separator by means of a 2″ diameter pipe attached to the bottom, and it left the separator on the side near the top.

The electrode, consisting of a cylindrical series of fine wires mounted on the circumference of cast-iron discs, was cemented into a 3″ nipple, this nipple being screwed into the top flange of the extractor.

Gas at the rate of 11.2 cubic feet per minute was admitted into the extractor, thus causing the suspended particles in the gas to be in contact with the electrical field for a period of 4.7 seconds, the current used amounting to 1.2 milleamperes at 10,000 volts, which was sufficient to remove all of the tar carried by the gas into the extractor.

This experiment was followed by another of greater capacity in which the extractor consisted of an inverted "U" made of 8″ cast-iron pipe and tees, the electrodes being attached to the tops of the pipes. These electrodes were four inches in diameter and were strung with 16 No. 27 steel wires, each electrode having an effective length of 5 feet 8 inches.

Twenty-eight thousand cubic feet of gas were passed into the extractor per hour, and if the entire cross-section were free of obstruction, the speed of the gas would be 22.6 feet per second, giving the suspended particles a contact period of 0.5 second in the electrical field. If the space outside of the electrode only is considered, the speed of the gas would be 30.2 feet per second, and the contact period 0.38 second.

The difference in potential between the electrode wires and the pipe forming the extractor, the latter being grounded, was maintained at 20,000 volts, with a current consumption of 2.6 to 3 milleamperes, while the watt-meter on the input side of the transformer varied in its readings from 200 to 230 watts, it being stated that the results, as regards tar removal, were very satisfactory.

TAR PRODUCTS

The many valuable tar products, so much in demand at present, are secured by distilling the raw tar into its various constituents in stills of either the vertical or horizontal type, the former finding great favor in Europe, while the latter is used to a large extent in this country.

Before running the raw tar into the still, it should be subjected to some character of dehydration process, and while many processes have been proposed to accomplish this, the following two methods are those most extensively used. In the one case the raw tar is subjected to a prolonged rest in large reservoirs, followed by a centrifugal separating process, as explained on page 15, and in the other it is pumped into stills of large dimension until the tar begins to flow from a cock located immediately below the top dome, after which the flow of tar is stopped and the still is subjected to heat.

The heat applied to the still causes the tar to become very thin before it reaches the boiling point, the greater portion of the water being collected on the upper surface of the thin tar and, as the heating continues, the level of the liquid is caused to rise above the overflow cock, thus allowing the water to be drawn off from time to time by opening the water cock; any vapors which may be produced during this heating process are passed through a condenser and recovered.

The vertical type of still is to be preferred over the horizontal, as its rate of evaporation is more rapid; this difference in time of evaporation causes about one-half the amount of fuel to be consumed per unit of tar distilled in the vertical still as compared with the horizontal, but it has many operating disadvantages not inherent in the horizontal type.

The vertical still and its apurtenances is shown in Fig. 9a, while the horizontal type is shown in Fig. 9b. The vertical still is usually constructed of a diameter about equal to its height, the shell being supplied with a concave bottom and a domed top, both the bottom and the top being constructed in sections for the purpose of adding strength to the structure and to facilitate repairs.

The concave bottom is not sprung directly from the lower end of the shell, but it is curved into a channel groove, the outer

upper edge of this grease being attached to the shell. The concave bottom considerably increases the heating surface of the still, and it also permits the metal to expand and contract with ease. The direct flame does not come in contact with the still bottom, this being protected by a brick arch, but the hot gases reach the bottom and lower half of the still through flues built into the brickwork for this purpose.

The horizontal still is set in brickwork as shown in Fig. 9b, and it is heated on somewhat less than half of its cylindrical surface, the metal being protected by an arch immediately

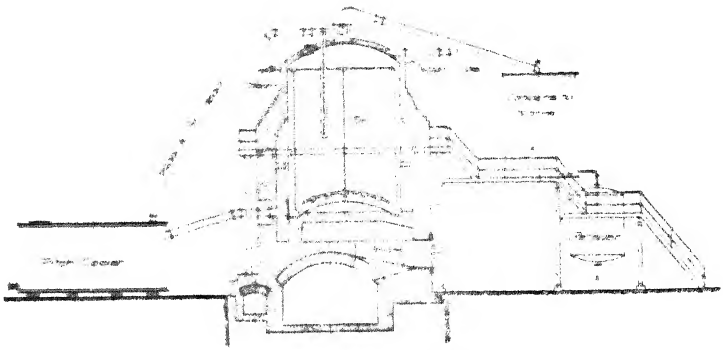


Fig. 9a.—Vertical Still.

above the fire and so designed that the portion of the shell subjected to heat may be quickly replaced if damaged.

All exposed portions of stills should be lagged; this is not only on account of the saving of fuel, but it also prevents undue corrosion, because the latter is prone to occur with great rapidity at points where excessive condensation is possible.

The condensing tanks for the condensing worms are made of either cast or wrought iron, and may be of any shape suitable for the purpose. These tanks are provided with a drain cock for the purpose of running off the water when required for repair purposes, while an outlet is provided near the top to permit the cooling water to escape during the first period of distillation.

The condensing worms consist of a series of coils of either cast iron or wrought iron pipe, the latter being preferable, owing to the more rapid transmission of either heat or cold.

From the coke oven the tar flows to the receiving or separating vessels. The tar separator, one of which is provided with each coke oven, consists of a large cast iron or steel vessel to conduct the different installations to the storage vessels.

Each still should be provided with a pitch cooler, usually a cylindrical tank from which the cooled pitch is run into the pitch bay.

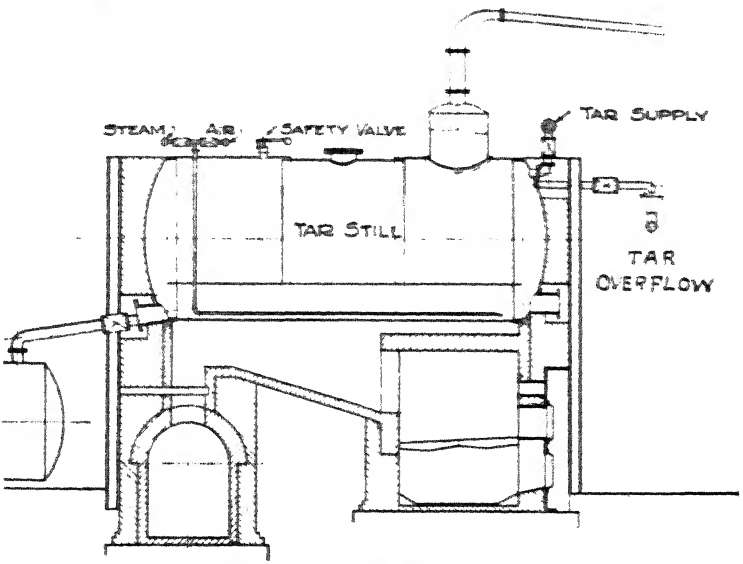


Fig. 9b — Horizontal Tar Still.

The fuel used under the still may be either coal, coke, or producer gas, the latter permitting of better control of the distillation process and therefore being preferred to the solid fuel.

When the still is properly charged, and all connections are found clear, the firing is started, especial care being exercised during the first period of heating to prevent priming or boiling over. When the tar is thoroughly heated and drops of distillate appear at the ends of the condensing worms, the heating is somewhat lessened, and great caution must now be exercised, as it is during this period when priming or boiling over usually occurs. If the still should prime the fires must be dampened and cold water poured on the dome of the still, this procedure usually stopping the trouble.

The first portion of the distillate is ammonia water and crude naphtha which passes from the collecting vessel into a separator, where the oil is separated from the water by difference in gravity, the water going to one side and the oil to the naphtha receiver. The temperature can now be raised a little as the volume of water becomes less. This first fraction, known as "light oil," comes off at between 70° to 170° C. (158° to 338° F.), and is run into the light oil receiver. During the production of this fraction the water in the condenser tank should be kept cold.

This fraction is usually about 3 per cent of the whole, and the intermediate products produced from it are Benzene, Toluene, and Xylene, while the crude commercial products are Benzol and Solvent Naphtha used as solvents, paint thinners, motor fuel, and gas enrichment. The intermediate chemical products are Nitrobenzene, Aniline Salts, Aniline Oil, and Carbolic Acid, while the refined chemical products produced from these are the Nitrotoluenes, Diphenylamine, other explosive ingredients, Aniline Dyes, Hydroquinone, and other photographic developers, as well as drugs and medicines.

The distillate coming from the worm will now be practically free of water, the fire is gradually increased, and the distillate is thus kept running at an even rate. The flow of cooling water through the condensing tank is cut off, and the temperature of the water in the tank is gradually allowed to increase by absorbing heat from the distillate as the latter passes through the worm. The condenser tank is provided with an open steam connection to permit of increasing the temperature of the water when heat absorption from the condenser worm is not sufficiently rapid to produce the required results. This necessity for heating the water is due to the increasing quantity of naphthalene salts in the distillate, and the worm must therefore be kept warm to prevent the deposit of the salts and the consequent choking of the worm coils.

This second fraction is produced between 170° and 230° C. (338° and 446° F.) and at the end of the period it is again cut, this second fraction being known as "middle, or dead oil," and the run of the succeeding distillate is diverted to the next receiver.

The intermediate products from the middle oil are Phenol, Cresols, Naphthalene, and Heavy Hydrocarbons. These inter-

mediates in turn produce Creosote Oil, Lamp Black, and some disinfectants. The intermediate chemical products are Carbolic Acid, Picric Acid, Phthalic Acid, Naphthols, Naphthylamines, and Salicylic Acid, while the refined chemical products consist of Picric Acid, Picrates and other Nitro-compound explosive ingredients, Naphthol dyes and colors, Indigo, and refined Carbolic Acid.

The yellow color of the distillate now increases and the odor of hydrogen sulphide predominates; the intensity of the fire is again increased and the temperature of the water surrounding the condensing worm is also allowed to increase. This cut is taken off between 230° and 360° C. (446° to 680° F.) and is known as Heavy, or Anthracene Oils. Another cut is sometimes made at this point, the first between 230° and 270° C. (446° and 518° F.) and the second above 270° C. (518° F.). At the end of this fraction some trouble may be experienced by the oil, while cooling, becoming solid, due to the presence of naphthalene salts, and the water in the condensing tank must be brought to the boiling point.

As the distillation proceeds the fire is slackened and steam is introduced into the still, this procedure lengthening the life of the still and also somewhat reducing the time required to distill the tar. The time for admitting the steam as well as the time for stopping operations cannot be pre-determined, as it depends on the character of the tar distilled and upon the character of the pitch required.

The intermediate products due to this fraction are Cresols, Naphthalene, Anthracene, Heavy Hydrocarbons, and Quinoline Bases, which in turn give Creosote Oil, Lamp Black, Road Oil, Timber Impregnators, Roofing and Paving Tars as crude commercial products, the intermediate chemical products being Anthraquinone and Alizarin.

Above 360° C. (680° F.) the residue is pitch, amounting to about 65 per cent of the total tar. Owing to the heat still stored in the still after operations are completed, the pitch residue is retained in the still for several hours, after which it is run into the coolers and from there into the pitch bay, where it is allowed to solidify.

The above fractions and the temperature of "cutting" are taken from an average sample of tar, but the three kinds of coal tar produced vary greatly in their characteristics. Horizon-

tal retort tar is the heaviest, and contains a low percentage of oils and a high percentage of pitch, while its "free" carbon content is also high. Coke-oven tar is lighter than that from horizontal retorts and contains a higher percentage of oils and a lower one of pitch. Vertical retort tar is the lightest of the three, and contains more oils and less pitch and "free" carbon than do the others.

From these differences it will readily be seen that the chemical constituents also vary greatly, and that the quantity of any particular constituent evolved from the tar will depend upon its original constitution.

Continuous distillation has also been tried both in Europe and in this country, and while success has varied in different localities, encouraging results have lately been announced, the principal systems being those of Hirzel, Kubierschky and Borrmann, Sadewasser, and Raschig, all of these having been devised in Europe.

In the Hirzel system two or more small direct-heated stills are employed, a thin layer of tar flowing over the hot bottoms of the stills. The first still drives off the ammonia water and light oil, the middle oil being produced in the second still, and the heavy oil in the third, providing the tar is to be fractionated in this manner, while soft pitch leaves the last still in a continuous stream. Distillation in this case is effected by the use of superheated steam.

The process devised by Kubierschky and Borrmann causes the tar to flow in continuous finely divided jets down a column against a counter-current of superheated steam, in the presence of which the high-boiling oils evaporate at a comparatively low temperature. The resultant composition of the vapors of course depends upon the ratio of the vapor tensions of water and the oils at any temperature.

The tar in Sadewasser's process is highly heated in a direct-heated tubular superheater, superheated steam being used as the heating medium; the heated tar from the superheater is forced through a spray nozzle into a vacuum vessel, entering the latter in a finely atomized state, thus causing the tar particles to volatilize immediately. Liquid pitch is first drawn off, followed upon cooling by the crude heavy and middle oils, and finally by the light oil and ammonia water.

In the system devised by Raschig three stills are employed, the first two being heated by steam and the third by hot water, but neither the steam nor the hot water comes in contact with the tar to be distilled. In the first still the ammonia water and light oils are driven off under atmospheric pressure, while the middle oil is driven off in the second still under a vacuum. The third still, also under vacuum, volatilizes the constituents forming the heavy oil, and the liquid pitch runs off from this still in a continuous stream.

The demand for coal-tar products, to be used in the production of explosives, dyes, perfumes, and drugs, has been brought home with ever increasing force to all gas works and coke-oven operators, and in order that these operators may consider the immensity of the proposition, and that every faculty must be strained to the utmost at the present moment to give the Nation what it requires, some of these finished products are briefly described below.

The total consumption of artificial dyes in the world attained a value of $92,000,000 in 1913, the United States consuming about $12,000,000 worth of the total. Of this latter amount about $3,000,000 worth was produced domestically, chiefly, however, from imported raw materials; $7,850,000 worth was imported from Germany; $910,000 worth from Switzerland, and $370,000 worth from Great Britain and France.

The outbreak of European hostilities put a stop to these imports, and we were consequently thrown upon our own resources to supply this much needed commodity, in many cases being compelled to go back to mineral, vegetable, and wood dyes, the production of which had been greatly reduced after the advent of the aniline product, and this need has therefore given a tremendous stimulus to the coal-tar chemical industry.

As stated above, this industry does not only include the manufacture of dye-stuffs, but also quite a number of very valuable drugs and medicines, besides the high-powered explosives.

The industry as a whole is based upon the use of about 10 crude compounds which are removed from the original tar in combination with some 150 other substances, being separated from the latter by fractional distillation. These 10 crude compounds produce about 300 very complex substances from which about 900 dyes, besides the drugs, explosives, and perfumes are

made by means of refined and complicated mechanical and chemical processes.

We have an abundance of raw material in the form of tar available, but a rapid development of this industry cannot be expected unless an effective law protecting the home manufacturer against ruinous competition by foreign makers is given by Congress.

The advent of aniline dyes has been of the greatest value to our cotton manufacturer, for while silk and wool yield readily to vegetable dyes, the inert character of the cotton fiber to assimilating the colors of vegetable origin, and the difficulty presented in mordanting cotton with metallic salts, caused our cotton fabrics to be limited to but a few colors. The aniline color dyes directly, without a mordanting substance on the cotton fabric, and has thus led to the present enormous development of colored cottons.

The 10 crude substances mentioned above are benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene, methyl anthracene, phenanthrene, and carbazol, while the principal "intermediates" are aniline oil, aniline salts, pure aniline, toluidine, nitrobenzol, naphthol, phthalic acid, salicylic acid, resorcin, anthraquinone, and many others up to the number of about 300.

Benzene and its homologues, toluene and xylene, besides being fractionated from tar, may be washed directly from the gas, and the same also holds good for naphthalene. The fractionation process as explained above produces four principal substances, namely Light Oil, Middle Oil, Heavy Oil, and Pitch, the distillation of 100 tons of bituminous coal giving on an average of 34 gallons of light, 205 gallons of middle, 100 gallons of heavy oils, and 8400 pounds of pitch.

The 34 gallons of light oil give $12\frac{1}{2}$ gallons of benzol, 186 pounds of naphtha and residues; the benzol in turn producing 5 gallons of benzene, $1\frac{1}{2}$ gallons of toluene, and 6 gallons of residues.

The 205 gallons of middle oil give 1512 pounds of fuel oil, 522 pounds of naphthalene salt, which in turn give 261 pounds of naphthalene, and 261 pounds of residues, and 168 pounds of crude phenols, the latter producing 37 pounds of carbolic acid, 56 pounds of cresylic acid, and 74 pounds of residues and losses.

The 100 gallons of heavy oils produce 928 pounds of green oil, and 186 pounds of anthracene cake, the latter giving 19 pounds of anthracene and 168 pounds of residues and losses.

The transformation of the ten crude coal-tar products into the "intermediates," is based on eleven processes, or

1. *Nitration:* This process requires that an aromatic compound shall be treated with a mixture of nitric and sulphuric acids, this treatment usually resulting in one, and sometimes two or three, atoms of hydrogen being replaced by the nitro group NO_2. The factors of time, temperatures, and proportion of mixture largely effect the extent and nature of this reaction, and results, besides the main product, in producing a residual in the form of dilute sulphuric acid which can be concentrated and used over again.

2. *Chlorination:* Chlorination is dependent upon the action of dry chlorine gas, but this reaction is not so readily controlled as is nitration, the end result often producing quite a variety of substitution products which are very difficult to separate. The residual in this process consists in the recovery of approximately one-half the chlorine used in the shape of hydrochloric acid.

3. *Sulphonation:* This process is dependent upon the action of fuming sulphuric acid, a large excess being usually employed; while this reaction is usually more readily controlled, it often results in the production of a variety of sulpho-acids which require separation, and uses for the discarded products is often a problem. The excess sulphuric acid is lost.

4. *Reduction:* Reduction consists of substituting hydrogen for oxygen in the nitro-compounds, thus forming the corresponding amido-bodies. For instance, benzol is changed into nitrobenzol by nitration, this latter product being then reduced to amidobenzol, or aniline, by the reduction process. The usual reducing agents consist of iron borings and filings, in conjunction with sulphuric or acetic acid.

5. *Oxidation:* The usual reagents employed in this process are chlorate or bichromate of potassium, lead peroxide, manganese dioxide or a permanganate, in conjunction with sulphuric or hydrochloric acid. Useful residues in the shape of potassium chloride, chrome alum, and several others usually result.

6. *Fusion:* The operation of caustic fusion is usually performed with sulpho-acids, resulting in replacing the sulpho-

group by hydroxyl. As an example, when benzol monosulphonic acid is fused with caustic soda, it results in the production of phenol. This operation is quite difficult, and requires great care, the results secured often being quite variable.

7. *Alkylation:* Alkylation consists of introducing the radicals methyl or ethyl, present in both grain and wood alcohols, into the hydroxyl- or amido-groups. This operation is conducted at elevated temperatures and pressure in autoclaves, hydrochloric acid in conjunction with the alcohols, or methyl or ethyl chloride, being used as reagents.

8. *Liming:* Lime or chalk is used to effect separations in mixtures through the varying solubilities of the calcium salts, this holding especially good for the sulpho-acids. It is also used to decompose chlorides and thus to effect the separation of resultant acids and aldehydes.

9. *Condensation:* This process embraces a large number of operations in which two molecules of different substances, or of the same substance, unite to form a new compound, with the consequent elimination of ammonia, water, or hydrochloric acid, sulphuric acid in excess being the usual condensing agent. Chlorides of zinc, antimony, sulphur, aluminum, and phosphorus are also used as condensing agents.

10. *Carboxylation:* This process consists of introducing the acid carboxyl group, by the combined action of caustic soda and carbon dioxide on phenol and its homologues. As an example, the carboxylation of phenol produces salicylic acid.

11. *Diazotizing and Coupling:* The diazotizing process is based on the fact that an aromatic amine will react with nitrous acid and produce a diazo-compound, while the coupling operation requires that the diazo-compound in the presence usually of sodium acetate will readily unite with quite a number of aromatic substances. This reaction splits up a product and yields the original amine and the amido-derivative of the second substance employed. As an example, salicylic acid when coupled with a diazo-compound, and then subjected to reduction, will be changed into amido-salicylic acid.

In the above eleven processes I have attempted to explain the chemical transformation required to produce the intermediates from the crudes, but besides these principal chemical changes there are many minor ones, as well as quite a number of

mechanical operations, such as precipitating, filtering, baking, boiling, and blowing off.

These processes result in producing 17 separate chemical classes, from which 921 dyes are produced, and it may be well now to refer to some concrete example of dye production.

Of all the coloring matters employed by man it is an assured fact that indigo is probably the oldest and most valuable, and it is recorded that the blue ribbons, removed from the wrappings of mummies over 5000 years old, were colored with indigo. Indigo, as formerly employed, was secured from indigo plants, and many India merchants made fortunes in days gone by from its importation, but the synthetic production of this product came on the market in 1897, and it has practically displaced the plant product entirely. Prof. Adolph von Bayer, of Munich, was the leading spirit and master mind in its final production, and he and his students labored on this subject for almost half a century. Before Bayer began his monumental task it was known that the oxidation of indigo would convert it into isatin, and that the distillation of indigo with potassium hydroxide would produce aniline; also that fusion with the same alkali would produce anthranilic acid, and that nitric acid would produce nitrosalicylic and picric acids.

All of these products resulted from the disintegration of the indigo molecule, and this led to positive knowledge that indigo blue contained a benzene ring, and that both carbon and nitrogen in neighboring positions to each other were attached to this ring. Isatin then being a product of the oxidation of indigo, Bayer reasoned that by a reverse process of reduction he could cause the indigo molecule to form again. His original attempts proved fruitless, but during the procedure he discovered other substances, such as indol, oxindol, and dioxindol. He firmly believed that indol was a close relative to indigo, and thought that by starting with the substance which had given him indol he could form indigo blue by some modification in his former process.

This modification consisted in an attempt to secure the indigo molecule through isatin instead of indol as the intermediate step, and although he failed to secure indigo blue by simple reduction from isatin, he was successful with the use of acetyl chloride, phosphorus trichloride, and phosphorus. A great many inter-

mediate steps were followed, and finally after 15 years of research he had accomplished one of the greatest triumphs in synthetic chemistry.

Since Bayer's original discovery, four different methods have been devised for producing indigo, three of these starting with benzene, and one with naphthalene. The usual procedure with benzene consists in first nitrating the benzene to form nitrobenzene, which is reduced to aniline; the aniline is then treated with chloracetic acid to form phenyl glycine, this product being then fused with sodium oxide to form indoxyl, which is finally blown out with an air blast to form indigo.

If naphthalene is used to start with, it is first necessary to oxidize the naphthalene to phthalic anhydride, this product being treated with ammonia to form phthalamid; by the action of sodium hypochlorite on the phthalamid, anthranilic acid is formed, which in turn is treated with chloracetic acid to form phenyl glycine, and carboxylic acid; this is now fused with caustic soda to form indoxyl, and the air blast again gives indigo.

The manufacture of magenta is due to benzene and toluene. The toluene is nitrated to form o- and p-nitrotoluene, this being reduced to o- and p-toluidine. The benzene is nitrated to form nitrobenzene, and is then reduced to aniline; this aniline is now treated with o- and p-toluidine, and o- and p-nitrotoluene, or the toluene products, to form the magenta base; the latter after being treated with hydrochloric acid forms magenta dye.

Hydroquinone, so much used in photography as a developer, starts with benzene, which is nitrated to form nitrobenzene, the latter being reduced to aniline, oxidized to quinone, and then reduced to hydroquinone.

In the manufacture of the high-powered explosives we find the nitro-substitution products of the coal-tar derivatives used as bursting charges for explosive projectiles, torpedoes, mines, detonators, and primers. They are also used in low freezing or non-freezing mining explosives, in plastic explosives, and in other types for the purpose of imparting some desired characteristic.

The two high-powered explosives depending upon coal-tar products most commonly used are picric acid and trinitrotoluol.

Picric acid, besides being an explosive, is also a yellow dye, and is principally used on wools and silk.

In the manufacture of picric acid, phenol or pure carbolic acid is used as the base; an equivalent weight of concentrated sulphuric acid is mixed with the phenol, and this mixture is heated to slightly above 212° F., after which it is allowed to cool slowly; after cooling it is dissolved in twice its weight of water, and then slowly added to three times its weight of nitric acid, the nitration being completed by heating after all fuming has ceased. This final mixture is allowed to cool very slowly, thus permitting the picric acid to crystallize out, after which it is purified by washing with warm water, and then re-crystallized.

Picric acid, as an explosive proper, has its disadvantages, as, due to its acid nature, it readily combines with the metals with which it may be in contact, thus forming picrates which are more sensative to percussion and friction, often causing a shell containing the picric compound to explode by a jolt while being transported. The melinite used by France, the lyddite used by England, and Shimose powder used by Japan are all picric-acid products.

Trinitrotoluene, another nitro-substitution product produced from coal-tar derivatives, although much more difficult to manufacture, is by far a safer explosive to store and handle, and it forms the base of the explosives used by Germany, although the other countries are also using this compound to some extent at present.

This explosive is produced by first converting the toluene into a mononitro-compound, after which it is treated with nitric acid at a slight increase in temperature, thus converting the mononitro-compound into dinitrotoluene, after which the latter is nitrated with concentrated nitric acid in a sulphuric acid solution, the final product thus formed being trinitrotoluene. This compound is also produced from orthonitrotoluene by means of a sulphonating process similar to that used in the production of picric acid, after which it is nitrated and crystallized, the resultant crystals being then purified in alcohol; this product is re-crystallized to the final compound, the alcohol being removed in a centrifugal hydro-extractor.

The manufacture of synthetic perfumes, while still in its infancy, has nevertheless found a great deal accomplished in this line, but much remains to be done. One of the most widely used perfumes is vanillin, which is synthetically prepared and

which is identical in composition with the vanillin extracted from vanilla pods. Other perfumes coming under this head are heliotropine, essence of bitter almonds and aubepine, these perfumes also being identical in chemical composition with the same perfumes obtained from plants.

A different category exists, however, covering perfumes which chemically have nothing in common with the natural product, artificial essence of violet being a prominent example of this class, and the discovery of this compound opened a wonderful path for the chemist in that he has found it possible to manufacture a perfume which has an odor identical with nature's product, but which in its chemical composition differs entirely. Another perfume of this class is artificial musk, this latter product having almost entirely supplanted the natural article. Artificial geraniums also come under this classification.

Light tar oils, with their content of benzene, are of prime importance in the perfumer's art; the benzene is converted into nitrobenzene, which in turn yields essence of mirbane with its odor of bitter almonds. Toluene is convertible into benzoic aldehyde, or essence of bitter almonds, identical with nature's article found in peach kernels, cherries, and cherry laurel leaves. This product can be converted into cinnamic aldehyde, the latter being the chief constituent of Chinese or Ceylon essence of cinnamon. It has a strong cinnamon odor, but by reduction it yields cinnamic alcohol, or artificial hyacinth.

Other constituents of light oils, such as the cumenes and xylenes, form the basis of the perfume manufacturers' art. Para-cumene is identical with that in the essence of thyme, and metaxylene is converted into artificial musk.

With the use of the middle oils, containing phenol, we are able to produce artificial geranium, or phenyl oxide, by a direct catalytic process, and the cresols, also by catalytic action, give cresol oxides, also of geranium odor. By mixing phenols and cresols various geranium odors are produced, but the process is rather difficult.

B-naphthol, in conjunction with methyl and ethyl alcohol, by a catalytic process yields yara-yara and neroline respectively, and this forms the base for the so-called Eau-de-cologne.

Salicylic aldehyde, produced from phenol by the action of potash and chloroform, also forms an important perfume, and

methyl salicylate is the essence of wintergreen, while salicylic aldehyde, when acted upon by acetic anhydride, gives coumarine, a remarkably soft perfume.

The mention of the above will demonstrate the importance of coal-tar derivatives for manufacturing perfumes, but a great deal remains to be done in order to place this industry on the same plane with the manufacture of coal-tar dyes.

In the manufacture of drugs, starting with benzene, we find that the latter yields phenol, diphenol, chloronitro-benzene, and aniline. The phenol in turn yields salicylic acid, which gives us salol, the salicylates, methyl salicylate, and aspirin; paranitrophenol, which gives phenacetine; orthonitrophenol, which gives guaiacol and thiocol; oxyphenyl-arsenic acid, which gives 606 or slavarsan; chlorophenol, which also gives guaiacol. The diphenols produce resorcin and pyrocatechine, the latter giving guaiacol. The aniline produces phenylhydrazine, which in turn gives antipyrin and pyramidon; from aniline we also secure piperazine, acetanilide, exalgin, and atoxyle, the latter also giving 606 (arseno-benzol), and hectine. Then diethyaniline, which gives novocaine, and dimethylaniline, which gives stovaine and alypine.

Toluene is converted into benzoic acid and benzaldehyde. The benzoic acid produces eucaine, stovaine, phthaleine, amidobenzoic acid, which in turn gives novocaine and orthoform; benzonaphthol, and cryogenine. The benzaldehyde gives cinnamic acid.

Naphthalene gives us benzonaphthol, naphthol, and betol.

The manufacture of synthetic phenol, or pure carbolic acid, is being practised in connection with several gas or coke works, and this enterprise became of immense value when imports were stopped early in 1915. In 1913 the United States imported 4077 tons of this valuable article, and its synthetic production therefore became an absolute necessity, as the stock on hand soon became exhausted.

The manufacture of synthetic phenol embraces five separate and distinct processes, the benzene required being secured from coal-tar distillation or from a direct washing of the gas.

These processes are:

1st. — The sulphonation of Benzene to Monosulphonic acid, or Benzene Sulphonic Acid.

2d. — The conversion of the Benzene Sulphonic Acid into a Calcium Salt Solution.

3d. — The conversion of the Calcium Salt Solution into a Sodium Salt Solution.

4th. — Fusing the dried Sodium Salt with Caustic Soda, producing Sodium Phenolate.

5th. — Decomposing the Sodium Phenolate with a mineral acid to liberate the Phenol.

In the operation of a plant for the production of pure phenol, the benzol must first be purified by distillation and rectification, the pure benzene being then admitted into the sulphonating kettle (*D*, Fig. 9c), where it is treated with concentrated sulphuric acid from tank (*E*); fuming sulphuric acid cannot be used, as it is liable to change the character of some of the benzene, and also change some of the resultant monosulphonic acid into a mixture of meta- and paradisulphonic acids.

This resultant monosulphonic acid is next processed in the lime treater (*F*) with hydrated lime to form calcium sulphonate, the excess acid being rendered inert by excess lime; the hydrated lime is prepared in the vessel (*H*) and forced into the measuring eggs (*G*), passing from there into the lime treater (*F*).

The calcium sulphonate is now forced through the filter press (*K*), where the insoluble sulphate is retained and the filtrate run into the soda tank (*L*); sodium carbonate is dissolved in the dissolver (*M*) and admitted into the vessel (*L*), where it combines with the filtrate from the press (*K*) to form sodium sulphonate.

This liquor is now forced through the filter press (*N*), where the insoluble calcium carbonate is retained and the sodium sulphonate run into the concentrator (*O*); after concentration the liquor is admitted into (*P*), where it is crystallized, the crystals being ground fine in the mill (*Q*), after which they are ready for the fusion process.

The dried sodium salt is fused with caustic soda in the autoclave (*R*) in order to produce sodium phenolate, this melt being dissolved in (*S*), the resulting mixture being then treated in the acidifying tank (*T*), where sulphuric acid is added in order to decompose the phenolate, thus producing phenol with sodium sulphate as a waste product.

This latter mixture is now admitted into the separator (*U*),

SYNTHETIC PHENOL PLANT
(CARBOLIC ACID)

A Crude Benzol Storage	N Filter Press for Calcium Carbonate
B Benzol Still	O Soda Solution Concentrator.
B' Rectifying Column	P Crystallizer
B^2 Dephlegmator	Q Burr Mill
B^3 Condenser	R Autoclave
C Purified Benzol Storage	S Dissolver
D Sulphonating Kettle	T Acidifying Tank
D' Condenser	U Separator
E Sulphuric Acid Storage	V Washer
F Lime Treater	W Filter Press for Sodium Sulphate
G Measuring Eggs	X Carbolic Still
H Lime Tank	X' Still Condenser
J Pumps	Y Carbolic Distillate Storage
K Filter Press for Calcium Sulphate.	Z Carbolic Distillate Concentrator
L Soda Tank	Z' Carbolic Crystallizer
M Sodium Carbonate Dissolver.	Z^2 Carbolic Crystal Drying Table.

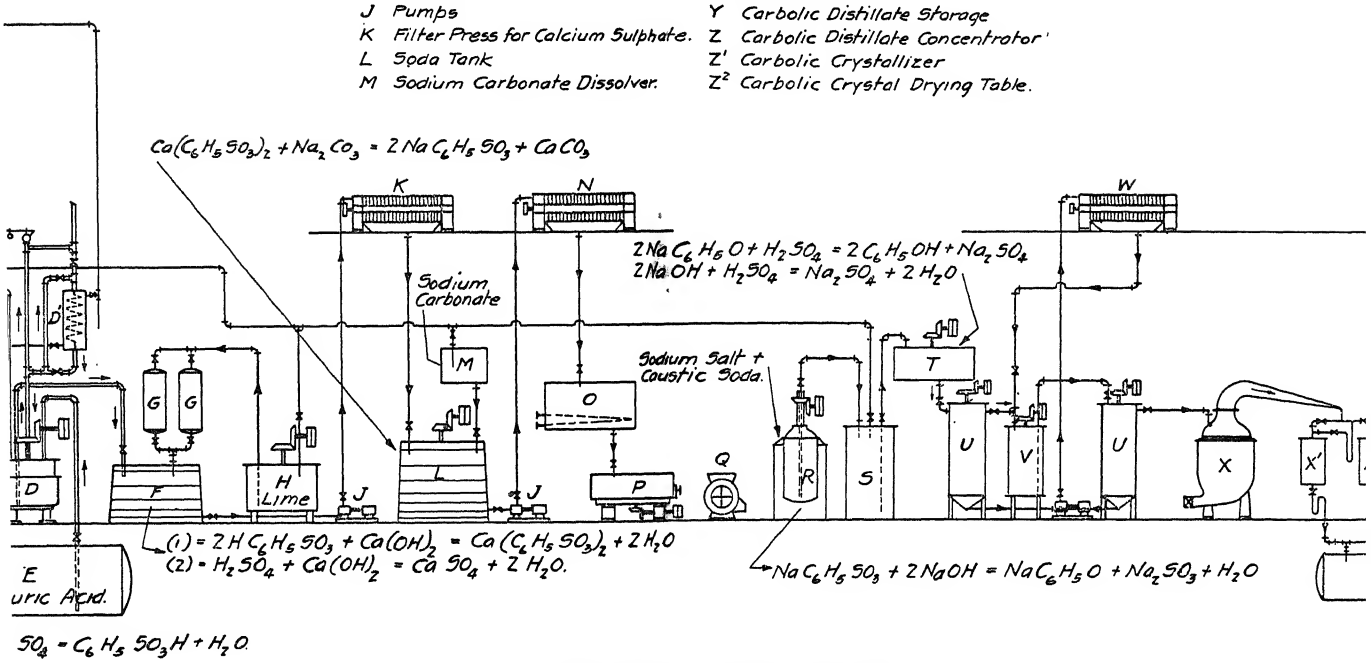


FIG. 9c.—SYNTHETIC PHENOL PLANT

the phenol, as well as the filtrate from the sodium sulphate press (W), being next run into the washer (V), the insoluble sodium sulphate being retained in the press while the washed solution enters a second separator (U) and passes from thence into the carbolic still (X).

The vapors from the still (X) are condensed in the twin condensers (X^1), and run into the storage tank (Y); the weak distillates from tank (Y) are forced into the double effect concentrator (Z), the concentrated solution being run into the crystallizer (Z^1) and, after being drained off, the purified crystals are placed on the drying table (Z^2), after which they are ready for packing.

From this it is seen that the raw material required to produce synthetic phenol is Benzol, Sulphuric Acid, Caustic Soda, Soda Ash, and Lime, and the amounts required to produce one ton of phenol are approximately:

Benzol	340 gallons
98% Sulphuric acid	4 tons
Caustic soda	1.5 "
Soda ash (sodium carbonate)	1 "
Slaked lime	2 "

During the process a sufficient amount of calcium carbonate is produced as a by-product to reduce the amount of lime given by about one-half. The other by-products recovered are about 3 tons of calcium sulphate (gypsum) cake, and about 3 tons of mixed sodium sulphite and sodium sulphate.

CHAPTER II

NAPHTHALENE

Naphthalene ($C_{10}H_8$) is a hydrocarbon and has a melting point of 174° F., a boiling point of 424° F., and it sublimes at lower temperatures. The deposition of naphthalene in a solid state in the mains or apparatus causes many operating difficulties, as it decreases the cross-sectional area of the gas conduits and thus produces considerable back pressure on the works.

The presence of naphthalene in the gas produced during the carbonization of coal, is undoubtedly due to the condensation or polymerization of paraffin hydrocarbons, particularly those of the Olefine or Ethylene series of the general formula C_nH_{2n}.

The synthesis of naphthalene, which is an aromatic hydrocarbon, from a paraffin hydrocarbon has been accomplished in laboratory investigation, and the similar synthesis of benzene and toluene by the Rittman process seems to give a further proof of such changes in constitution.

The fact that naphthalene is produced in varying amounts in both carbureted water gas and in oil gas, dependent upon the operating conditions, tends to substantiate its paraffin origin.

Naphthalene formation is influenced by the kind of coal used, the type of carbonizing chamber employed, and the degree of superheat to which the gas is subjected on exiting from the charge. In the older type of benches, viz., horizontal and inclined retorts, the gas is in contact with a considerable heated surface, and while the production of naphthalene may be reduced by working with heavy charges, its total elimination is impossible.

With the vertical retort systems, particularly those of the continuous type, this superheating effect is to a very great extent eliminated, since the gas passes through the core of uncarbonized coal, and little or no naphthalene is produced. The tar produced in these retorts is distinctive, as it contains paraffin

bodies significant particularly with the absence of naphthalene in the gas.

Attempts have been made to produce records showing the varying constitution of the gas in connection with high or low naphthalene content, but these are of little value, as at best they are only comparative but not absolute. In the same plant, any change in the operation of the retort house would naturally affect the quality of the gas, and it is therefore doubtful if adequate comparison on the basis of gas quality should be made between the gas from several retort systems in determining the amount of naphthalene that should be present.

Coal gas has a definite saturation for naphthalene, or in other words at a certain temperature it can carry a certain quantity of this impurity, and consequently if naphthalene is produced in the retort house, it will always be found in the gas.

The greater portion of the naphthalene produced, especially with high distillation or carbonization temperatures, goes over into the tar, the gas containing only a portion of the naphthalene vapor.

The amount of naphthalene required to saturate a gas varies according to different investigators, and Table IX

TABLE IX. — NAPHTHALENE SATURATION

Temperature		Grains per 100 cubic feet of gas	
Centigrade	Fahrenheit	Schlumberger	Allen
0°	32°	2.0	6.0
5°	41°	3.2	9.8
10°	50°	6.7	14.1
15°	59°	10.9	19.0
20°	68°	16.5	24.6
25°	77°	24.7	30.9

gives this saturation according to both Schlumberger and Allen.

The results of these two independent investigations vary considerably, but it is readily seen that a gas saturated with naphthalene must give up the latter with falling temperature.

For higher temperatures than those given in the table, the amount of naphthalene in saturated gas averages per 100 cubic feet at

90° F., 71.00 grains	100° F., 116.97 grains
110° F., 182.10 "	120° F., 276.23 "
130° F., 404.32 "	140° F., 629.62 "

The committee appointed by the American Gas Institute, 1913, to examine into the naphthalene problem made this the subject of exhaustive study, and the committee agrees with the statement that the production of naphthalene is a function of the temperature the gas assumes before it leaves the retort, rather than that of carbonization, and that gas works with ample condensing facilities are able to confine the naphathlene stoppages to the plants.

Naphthalene troubles begin in summer, and they are aggravated by light and irregular charging; a district once affected will give trouble for some seasons afterward through the gas mains storing up the naphthalene and the gas depositing it elsewhere. Efforts were formerly made to reduce the trouble by charging large percentages of cannel coal, and later by carbonizing petroleum in special retorts, although when the heats increased, the latter method caused the formation of more naphthalene. It was also found that the introduction of water gas in many cases made no differences in the deposits.

A list of 29 questions was sent to 16 different plants asking for particulars as to details of equipment, method of operation, and naphthalene troubles. From the replies received it appears that naphthalene is produced at all the works in question; the heats ran from 1850° to 2200° F., except at one coke-oven plant, where the rich gas during the first part of the carbonizing period leaves the ovens at 1200° F., and it is free from naphthalene, while the lean gas produced during the latter period of carbonizing leaves the ovens at 1800° F. and contains naphthalene in considerable quantities.

Two plants, a vertical retort system and a coke-oven respectively, produced a crude gas with a remarkably low naphthalene content, and hence depended entirely upon the tar, which was also low in naphthalene, to absorb it.

Conditions governing the hydraulic mains and the tempera-

tures in them, as well as the character of seals, dip pipes, etc., were also examined into, but without result. The condensing apparatus in the works answering the questions is of two types — the multitubular water-cooled condenser, and the cataract washer cooler. Either of these was capable of doing the required work, but the latter has the advantage over the other in being self-purging.

Three of the works reporting employ naphthalene extractors, two of the grid scrubber type and one a rotary washer. The solvent in all cases was water-gas tar, the amount used being 0.14 and 0.25 gallon per 1000 cubic feet of gas in two of the works respectively, and 0.05 for inclines and 0.072 gallon for horizontals in the third plant, the wash oils containing varying percentages of naphthalene up to 11.29. It was found that every water-gas tar is not suitable for the purpose, especially the tar produced at high temperatures and which is apt to be saturated with naphthalene, and therefore incapable of further absorption. Other tests indicated that absorption with anthracene was better at low temperatures than at high, and the same holds good for any solvent or absorbing medium.

Several of the works made use of steam and gasoline for clearing stoppages, but this is not good practice; steam will melt naphthalene, and gasoline will dissolve it, but the resulting liquid must be immediately removed, otherwise it will solidify and become so hard that nothing but a steel bar can touch it. A copious stream of boiling water is preferable to steam, and a heavy oil of low vapor tension to gasoline.

A study of the conditions covering the works in question led to the statement that in order to prevent naphthalene troubles, a system of carbonization should be selected in which the gas is exposed to as little secondary heating as possible; the gas, if possible, should be cooled in the works to a temperature as low or lower than it will meet outside, and then finish the gas by passing it through a naphthalene washer. By exercising extreme care, but little naphthalene will escape beyond the works, and a few grains can be taken care of in a mixed coal and water gas, or where benzol is used as an enricher. Where straight coal gas is made, a condenser at the outlet of the works might be considered with a view to removing moisture, in the absence of which naphthalene does not precipitate.

Another method for obviating this trouble is to introduce into the gas a sufficient quantity of the vapor of oils having a somewhat lower boiling point than that of naphthalene, and this method results also in a gain in candle-power and calorific value, besides requiring little attention and is fairly certain in its action. The drawback inherent in this method, however, is found in the pernicious action of the solvent deposited by condensation on the paint of gas holders and also occasional trouble with pipe joints, meters, and fittings due to condensation of the oil. Dr. W. B. Davidson states that the improvement of the quality of the gas treated by the addition of oil vapors is not always conceded, and that proper allowance should be made not only for candle and calorific value due to the oil vapors, but also for the increase in volume.

The solvents most commonly used for this purpose are solvent and heavy naphtha, crude heavy naphtha, condensed liquid secured during the compression of oil gas, light paraffin oil, and kerosene. Of these solvents, those derived from coal-tar or carbureted water-gas tar are probably the most efficient; if the condensate due to oil gas compression is used, an additional advantage is secured from the enriching quality of this product. If paraffin oils are used, they must be added to the gas in the shape of a mist, or in such a finely divided state that there will be no question of this mist being mechanically carried throughout the entire system, a difficult performance.

Present prospects point to the necessity of removing benzol and its homologues from the gas, as they are very necessary for the manufacture of explosives, and as these constituents become less, the more trouble can be expected from naphthalene; while the removal of benzol and toluol in themselves would not have a material effect on the absorption of naphthalene, the removal of these two constituents also effects the removal of higher boiling vapors, thus reducing the amount of solvents in the gas capable of taking up the naphthalene. In such cases where benzol is not extracted, from 10 to 15 gallons of solvent per million cubic feet will generally be sufficient to relieve the trouble, but in the opposite case the amount of solvent must be increased up to about 20 gallons.

The removal of the naphthalene at the works, or the addition of a solvent, will not entirely remove all troubles, providing the

distribution system contains naphthalene deposits, as although the gas may leave the works practically free of naphthalene, or if it contains sufficient solvent to prevent the naphthalene from crystallizing out, the gas will take up naphthalene from that in the mains. If this gas, carrying an increased burden of naphthalene, reaches a colder main, it will again deposit the excess of naphthalene beyond that which the solvents can hold, and this condition will continue until the mains have been cleaned out. These local deposits can be removed by spraying a solvent into the mains in the district affected.

Spraying a solvent into the gas must be done with care, and a spray must be selected which will produce a mist, and not large drops, as in the latter case it will not be carried with the gas for a distance sufficiently far to be effective. Care must also be exercised not to spray the solvent into a main near a sharp bend, as the impingement of the gas on the surface of the pipe at such points will act to strip the mist out of the gas.

If the solvent is to be vaporized, and not sprayed into the gas, the solvent is usually treated in an apparatus which embodies a large vaporizing plate, heated by steam, the solvent flowing over this heated plate in a thin stream. About 10 per cent of the gas to be enriched is by-passed and shunted through the vaporizer, the vapors of the solvent joining the gas in its passage, the mixture being then returned to the gas main in such manner that the flow of the mixture is in the direction of the gas flow, thus thoroughly mixing with the main volume of the gas and passing on with it.

If possible, the solvent should be given to the gas at a point between the station meter and the holder, this point having advantages over any others. The gas is practically constant in volume at this point, and the amount of solvent given to the gas need, therefore, not be varied during the day, while if it were added after the holder outlet, where the flow is irregular, due to varying consumption, the addition of the solvent would have to undergo constant regulation, owing to the differences in the volume consumed during various hours of the day. Besides this, if the solvent is added ahead of the holder, the deposition of naphthalene in the drips at the holder inlets and outlets will be prevented.

If the finished gas is a mixture of coal gas and carbureted

water gas, a less amount of solvent will be required than with straight coal gas, because the carbureted water gas usually contains a higher percentage of solvents than does coal gas of the same quality.

Washing the gas under ordinary conditions, 100 grammes of anthracene oil will absorb from 10 to 25 grammes of naphthalene, according to temperature, or 100 grains of anthracene oil will absorb from 10 to 25 grains of naphthalene, but before using this oil from 3 to 4 per cent of benzol should be added, this addition leading to greater extraction efficiency, this effi-

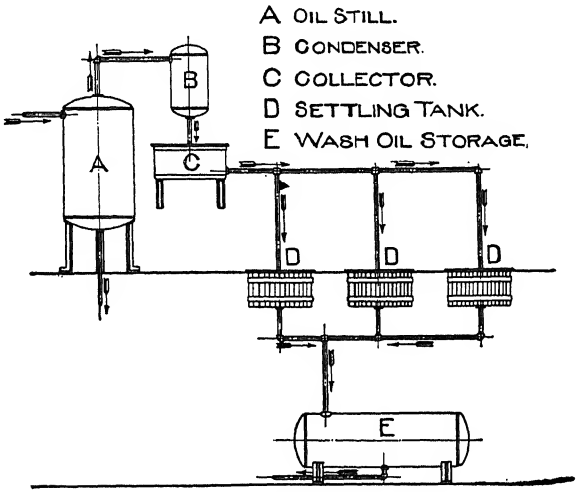


Fig. 10. — Oil Regeneration Plant.

ciency being further increased by thoroughly and slowly cooling the gas, as the absorption is most complete at a temperature of from 60° to 70° F.

Creosote oil, under ordinary conditions, has about the same absorption efficiency as anthracene oil, but in both cases the absorption will depend upon the amount of phenols present in the oil.

Water-gas tar will absorb from 18 to 20 per cent of its own weight in naphthalene, this absorption efficiency also being dependent upon the amount of phenols present in the gas.

In Germany it is usually estimated that anthracene oil will absorb about 40 per cent of its own weight in naphthalene, and as their gas usually contains about one gramme of

naphthalene per cubic meter, or 43.6 grains per 100 cubic feet, they use from 0.6 to 0.9 kilogram of anthracene oil per 100 cubic meters of gas, or 3.75 to 5.6 pounds of oil per 1000 cubic feet of gas.

If water-gas tar, or if water-gas oil is used as the absorbing medium, it can be run back to storage bearing its naphthalene burden, as the latter is not detrimental to the further use of the tar or oil, but if anthracene or creosote oil is used, this oil must be regenerated in order to fit it for further use; a diagram of a plant for regeneration is shown in Fig. 10.

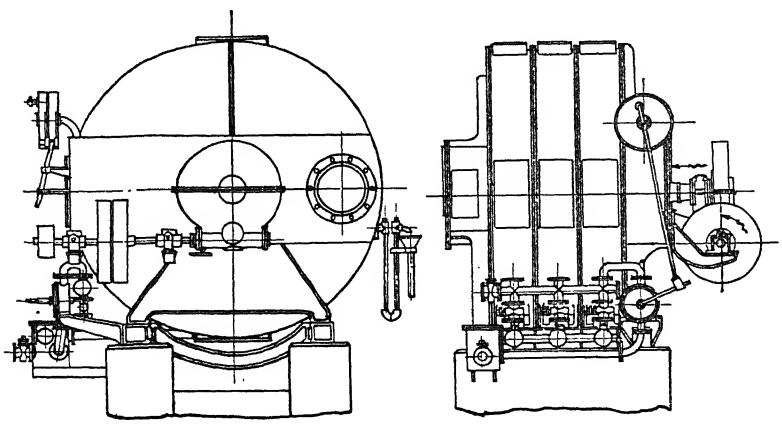


Fig. 11. — Horizontal Type of "Standard" Washer.

The saturated naphthalene absorption oil is run into the still (*A*), where it is distilled, the distillate being condensed in the condenser (*B*), the oil then entering the collector (*C*), from whence it flows into the settling tanks (*D*), where after complete cooling of the oil the naphthalene crystallizes out. The mother liquid is now free of naphthalene and it is run into the storage tank (*E*), from whence it is pumped back into the washers or it is stored for other disposition.

The removal of the naphthalene from the gas is usually accomplished in some type of mechanical washer, either of the Standard horizontal type, as shown in Fig. 11, or in the Feld vertical centrifugal type, shown in Fig. 12.

The Standard rotary washer is constructed of one double

chamber, three single chambers, and two or three double chambers, according to whether anthracene or creosote oil is to be used as a washing medium, the larger number of washing chambers permitting greater unit absorption. The wash oil enters the last chamber of the washer, where it meets the cleaner gas, and after a certain degree of ab-

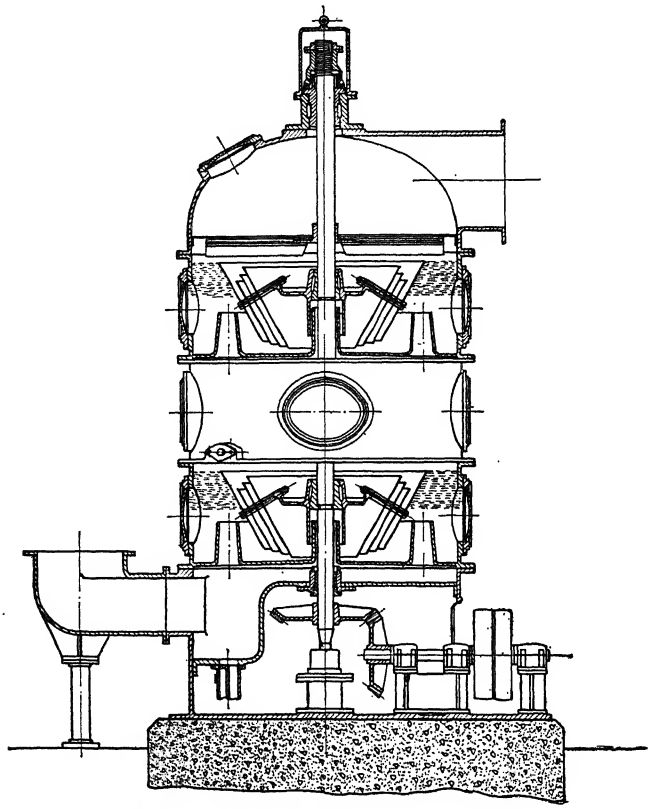


Fig. 12. — Feld Vertical Centrifugal Washer.

sorption has been obtained the oil is pumped into the next forward chamber, and so on until it is saturated, thence leaving from the gas-inlet chamber and flowing to the point of disposition. The chambers are interconnected with piping and cocks to a pump which receives motion direct from the revolving shaft of the washer proper.

In the Feld centrifugal washer (Fig. 12), the wash oil enters the top section through a syphon, being then pumped up on the inside of the spraying cones and hurled out through the perforations in a very fine mist or spray, thus filling the

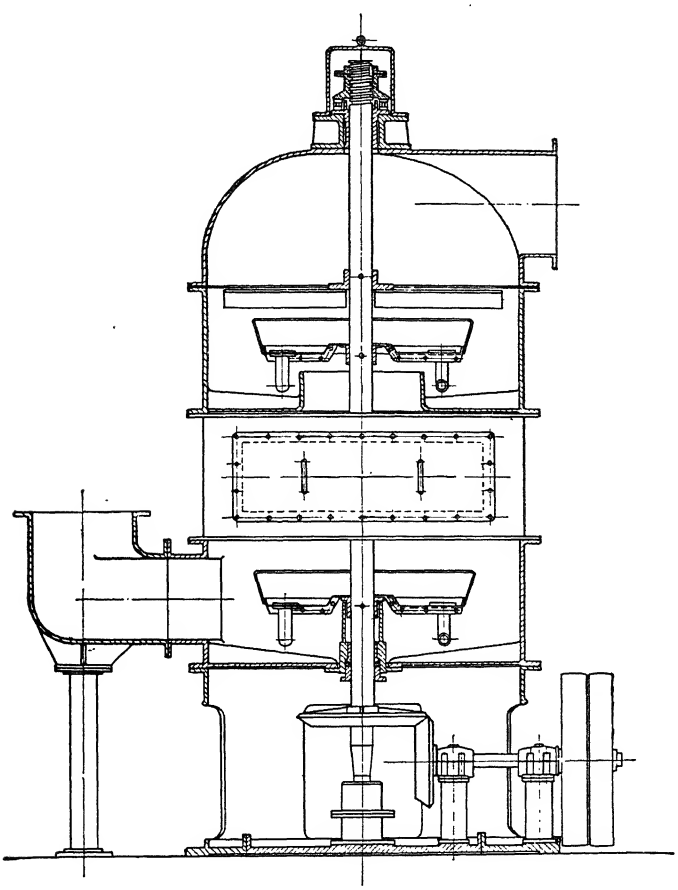


Fig. 13. — Vertical Type of "Standard" Washer.

entire gas space with a mist of wash oil; the oil after partial saturation flows into the next lower section through the gas ports, being again brought in contact with the gas in the same manner here, finally leaving the bottom of the washer in a saturated condition.

The action of the Standard centrifugal washer (Fig. 13) is similar to that of the Feld, but instead of revolving cones, the vertical shaft is provided with a perforated basket, the wash oil being picked up and sent to the basket by means of the bent tubes attached to its bottom.

The vertical centrifugal washers are more efficient than the slow-moving rotaries, because they do not depend upon skin contact for absorption, the oil in the verticals completely surrounding the naphthalene vapors and causing their absorption. The natural flow of the liquid being downward, no pumps are required for transferring the liquid from chamber to chamber, and as the inflow of wash oil can be regulated, the oil may be kept in the washer for any required period of saturation, the outflow of oil being entirely dependent upon the quantity of oil admitted into the top chamber of the washer.

The removal of naphthalene seems to be primarily a function of the gas temperature, as is seen from the following data secured at one of the large coal-gas works. As originally designed, the gas arrived at the naphthalene washers without any other cooling than that produced by the atmosphere around the overhead mains, this condition causing the temperature of the gas at the naphthalene washers to vary greatly with the season of the year and the amount of gas produced, the extraction results being given in Table X.

TABLE X. — NAPHTHALENE EXTRACTION

Gas temperature F.°	Grains naphthalene per 100 cu. ft. of gas		Per cent removed
	Washer inlet	Washer outlet	
134	229	156	32
113	121	70	42
91	61	17	72
87	39	14	64

This condition led to a great deal of trouble in naphthalene stoppages, principally in the condensers which immediately

followed the naphthalene and cyanogen washers, especially during the summer months, necessitating the installation of primary condensers between the exhausters and the tar extractors, the gas temperature being thereby maintained at between 85° and 90° F.; no further trouble due to stoppages was experienced since treating the gas at these temperatures, water-gas tar being used as the washing medium in the naphthalene washers with results as given below:

Water gas tar used per ton of coal	0.25 to 0.38 gallon
Saturated tar produced per ton of coal	0.25 to 0.37 gallon
Per cent of naphthalene by weight in saturated tar	12.71 to 18.60 %
Specific gravity of saturated tar at 60° F.	1.086 to 1.082
Naphthalene per 100 cu. ft. of gas at washer inlet	40.1 to 59.4 grains
Naphthalene per 100 cu. ft. of gas at washer outlet	23.3 to 21.1 grains
Naphthalene in water gas tar before using	Only traces

An attempt has lately been made to use naphthalene as fuel in internal combustion engines, and some success has been met with in this direction; the present drawback seems to be the fact that it is necessary to start the engine with gas or some liquid fuel, and so to operate it until the heat generated by the engine is sufficient to melt the naphthalene, after which the latter is fed to the engine, vaporized, and exploded. Complete success in this direction would soon open up another source of revenue to the producer of coal gas.

It may be interesting to state that a locomotive operating on naphthalene has recently been constructed in France; this locomotive is provided with four cylinders, each two cast en bloc, 5.5 inches bore by 8 inches stroke, 70 horsepower being developed at 950 revolutions per minute. This machine is provided with two carburetors, one used on starting with spirit, and the other for the naphthalene. The carburetor used in connection with the naphthalene is cast en bloc with the reservoir in which the naphthalene is melted, double walls for the circulation of cooling water being provided, the temperature of this water being maintained at 212° F., thus maintaining a constant melting temperature.

Naphthalene engines have been built in Germany for some

years, and these engines usually consist of a single, or at the most, a twin cylinder four-cycle horizontal machine, following in its principal lines the model of the Otto engine. Above or alongside the cylinder with its cooling jacket, there is a double-walled naphthalene fusing tank, from which a heated tube leads to the carburetor through a float valve and a sprayer inserted in the pipe supplying air to the cylinder.

The naphthalene fusing tank is heated by waste heat from the engine, while in the earlier engines the naphthalene was rapidly melted by the exhaust gases; this latter method was attended with the disadvantage that overheating and too free an evolution of vapor were liable to occur. The Deutz gas engine works adopted the plan of melting the naphthalene by the heat of the cooling water, and thus avoided overheating the naphthalene.

In the older Deutz engines the cooling jacket of the engine cylinder was connected with a large cooling water tank in which the water after a time came to a boil, the naphthalene receptacle being suspended in this tank, and the naphthalene being thus liquefied by the heat of the cooling water and the escaping steam. The hot water surrounded all the adjacent parts in order to prevent the melted naphthalene from solidifying; but even so, it was found that the naphthalene solidified in the sprayer unless the air supply had been previously warmed, and the heat of the exhaust gases was therefore used to raise the temperature of the air in the suction pipe to 250° to 300° F.

The later Deutz engines are provided with a small water-tube boiler, heated by the exhaust gases, and which boiler communicates with the cooling jacket of the engine, and so raises the temperature of the water to the boiling point more quickly after the engine is started than is the case when the cylinder heat alone is relied upon for the heating of the water. The naphthalene is thus melted more quickly than in the old type of engine. K. Bruhn reports the efficiency of naphthalene as compared with other fuels as follows.

Consumption at	Gasoline		Benzol		Naphthalene	
	Consumption oz.	Cost ¢	Consumption oz.	Cost ¢	Consumption oz.	Cost ¢
Half load....	16.6	4.32	14.1	2.88	13.4	1.10
Three Quarter load.....	13.1	3.36	10.6	2.16	11.3	0.94
Full load.....	11.3	2.88	9.5	1.92	10.2	0.84

CHAPTER III

CYANOGEN

Cyanogen (C_2N_2) is a gas composed of carbon and nitrogen, and it is probably produced during the period of carbonization in the form of hydrocyanic acid by the decomposition of some of the ammonia, due to contact with the hot coke in the retort, as per the equation

$$C + NH_3 = HCN + H_2,$$

and the amount of cyanogen produced by the carbonization of any particular coal bears a certain relation to the amount of nitrogen contained in the coal.

Cyanogen in its gaseous form is colorless and very poisonous. When in combination with potassium it forms potassium cyanide, which has found its largest application in the cyanide process of gold extraction, this process depending upon the solubility of gold in a dilute solution of potassium cyanide in the presence of air or of some other oxidizing agent, and it is best adapted for use with free milling ores after the bulk of the gold has been removed by amalgamation, thus recovering such portions as were not taken up by the amalgam, the gold being later usually separated from the cyanide solution by an electrolytic process, or some other metallic precipitation process.

Potassium ferrocyanide is the base of a great many cyanogen products, one of the principal ones of which is prussian blue; this coloring matter is obtained by mixing the potassium ferrocyanide with a solution of ferrous sulphate, a precipitate of ferro-potassic-ferrocyanide, having a grayish-white color, resulting, the mother liquor, which contains potassium sulphate, being removed from the precipitate by evaporation. After the precipitate has been allowed to settle, it is washed with a large amount of water, and then oxidized, this oxidation giving it the beautiful blue color required in the dyeing industry.

The amount of nitrogen going to the formation of cyanogen is problematical, and the tests as to the ultimate disposition

of the nitrogen, according to the different authorities, is given in Table XI, the coal used in carbonization containing from 1 to 2 per cent of nitrogen.

In these six tests Knublach shows the largest percentage, 1.80 per cent, as going to cyanogen formation, and Desmarets the lowest, or 1.30 per cent.

TABLE XI. — DISTRIBUTION OF NITROGEN

Nitrogen	Foster	Leybolt	Knublach			Desmarets
	%	%	%	%	%	%
In coke	49.90	33.75	30.00	35.60	63.90	33.00
In ammonia	14.50	12.00	11.90	14.10	11.60	13.50
In cyanogen	1.56	1.75	1.80	1.80	1.80	1.30
In tar	34.04	1.50	1.30	1.40	1.30	2.00
In gas		51.00	55.00	47.10	21.10	50.20

The removal of cyanogen from coal gas is of decided advantage for two reasons, viz.: it is an impurity which is very objectionable, and it is a valuable by-product under certain conditions. If cyanogen is permitted to pass on into the purifiers it will be found to enter into combination with the iron in the purifying material, thus rendering a certain portion of this iron inactive for hydrogen sulphide extraction; on the other hand, the sale of spent oxide containing a high percentage of cyanogen is more remunerative than if it contained only sulphur, as this oxide is often purchased on the basis of its "prussian blue" contents only, "prussian blue" being the name applied to this cyanogen combination.

In spite of the removal of a certain percentage of the cyanogen in the purifiers (there are also times when it is thus entirely removed), quite an appreciable portion passes on with the gas, and this cyanogen has a considerable corrosive action on all iron or steel with which it comes in contact; this is especially noticeable in the case of gas holders, where a blue color is often seen on the outside of the holder sheets, indicating that corrosive action is taking place.

Cyanogen passing on into the purifiers always produces an ammonia loss amounting to from $\frac{1}{2}$ to $\frac{3}{4}$ grain per 100 cubic feet if the oxide in the purifiers is to be kept in its most active form. This small amount of ammonia should be

retained in the gas in order that it may neutralize its acid qualities and thus maintain an alkaline state in the oxide, because this alkaline condition is conducive to the formation of ammonium sulphocyanide, due to a combination between ammonia and sulphur, this compound being removed from the boxes through the sealed drains, while if the gas should retain its acid character the cyanide-compounds would combine with the iron and form the double iron cyanide compound known as "prussian blue"; this latter compound is insoluble and it rapidly coats the oxide with a layer which is then impervious to the action of sulphur.

Many attempts have been made to produce a combination between the nitrogen carried in the cyanogen and hydrogen, with the object of forming additional ammonia; the most successful of these attempts seems to be the process developed by Mr. Charles Carpenter, of England, and the liming process, both of which claim an efficiency of 98 per cent. It must be stated, however, that up to the present the author does not know if the financial returns would warrant the application of either of these methods, and their further development is therefore awaited with great interest.

The revenue to be derived from the extraction of cyanogen from coal gas is dependent upon the amount of coal carbonized and upon the market price of the product, the latter fluctuating constantly; it is certainly not a remunerative proposition for works carbonizing less than 250 tons of coal per day, as the same labor expended on a plant of this size can readily handle the proposition in one of double the capacity.

The estimated revenue, prior to 1915, in a plant carbonizing 250 tons of coal at one works, and 750 tons at another, the sludge from both being worked up in the one plant, after deducting operating expenses and 6 per cent interest and 6 per cent for depreciation, amounts to $27,935 per year, and this without the additional revenue to be derived by the production of ammonium sulphate from the cyanogen press liquor, this liquor being sold on the basis of concentrated ammonia. Besides this revenue, the extraction of cyanogen in this case shows an added efficiency of 22 per cent in the action of the purifiers, or the life of the oxide is increased by 22 per cent.

If the cyanogen plant is combined with the direct sulphate

recovery plant, the revenue to be derived from a combined plant carbonizing as low as 250 tons of coal is unquestionable, as will be shown later.

The cyanogen process operated by the British Cyanides Company consists in washing the gas with ammoniacal liquor in combination with sulphur. In this case the ammonium sulphide present in the liquor dissolves the sulphur to form a polysulphide which reacts with the hydrocyanic acid in the gas and forms ammonium sulphocyanide, or

$$(NH_4)_2S_2 + 2HCN = 2NH_4CNS + H_2O.$$

This ammonium sulphocyanide is converted into either potassium cyanide or potassium ferro-cyanide.

The British Cyanides Company,[1] in developing its process, adopted a policy in contradistinction to that prevalent on the European Continent, in that they were not averse to the formation of sulphocyanide of ammonia, but stimulated the production of polysulphides of ammonia by washing the gas with gas liquor in which granulated sulphur was kept agitated, before it reached the ammonia scrubbers, and while it still contained hydrogen sulphide and ammonia in large quantity.

Polysulphide of ammonia is an active absorbent of cyanogen, and readily combines to form sulphocyanide of ammonia. The system of operation proved very simple, and the liquor thus obtained was sent to a chemical plant for conversion. This system was installed in a British gas plant in 1905, a "Standard" washer-scrubber, fitted with Holmes brushes being used. The sulphur was periodically admitted into the scrubber through gas-tight cups, but trouble was soon experienced with tar particles, from the gas, coating the sulphur, thus interfering with the necessary chemical reactions by preventing the gas from coming in contact with sulphur, and finally clogging the washer. This washer was replaced by two cast-iron machines designed for the purpose and consisting of one chamber above a lower one, the upper one being provided with a vertical rotating shaft carrying stirring paddles by means of which the sulphur was kept in a thorough state of agitation, the liquor overflowing from the upper into the lower chamber. The gas entered the lower chamber and, through the medium of dip

[1] A. E. Broadberry. "Jnl. of Gas Lighting." Oct. 1, 1912.

pipes, bubbled through the liquor contained in it, passing thence up a connecting pipe into the upper chamber where it again bubbled through the liquor contained in same. The upper chamber formed the polysulphide of ammonia, while the lower one extracted tar particles, in order to keep them from reaching the sulphur, and also dealt with any polysulphides which had not absorbed cyanogen in the upper chamber. This machine was successful except for the back pressure thrown, and occasional tar troubles.

Mr. P. E. Williams, engineer of the Poplar Station of the Commercial Gas Company, London, where Holmes washers were used for this process, found it desirable to try some other form of apparatus for the production of the polysulphides in order to relieve the washer of this portion of the work, and in 1909 he decided to make use of a special design of purifier box containing spent oxide, with about a 50 per cent sulphur content, kept in a moist condition by means of liquor sprays. The gas entered this box at the bottom, and was caused to bubble through the polysulphide liquor, kept at a given level in the bottom of the box, before it reached the oxide.

The object in using spent oxide was due to the desire to avoid purchasing sulphur, and it was anticipated that by combination with ammonium sulphide the sulphur contained in the oxide would gradually be absorbed. This apparatus proved very effective, and it was soon learned that it was not necessary to transfer the polysulphides, produced in the purifier, to the Holmes washer, as was originally intended, as the contact with the gas in the purifier was so complete as to cause the nascent polysulphides to combine with the hydrocyanic acid and thus immediately to produce the desired sulphocyanide of ammonia. The spent oxide was sprayed each day for about 20 minutes with water or liquor in order to maintain its moist condition.

It was at first presumed that the spent oxide, owing to its gradual loss of sulphur, would have to be renewed from time to time, but upon making a test on the material it was found that the sulphur content had slightly increased, due possibly to a decomposition of the hydrogen sulphide in the gas, thus not only adding its molecule of sulphur to the ammonium sulphide, but also leaving additional sulphur in the oxide.

Mr. P. E. Williams further reports that a reversal of the gas

flow for a very short period is beneficial, this reversed or down-current being for the purpose of allowing the supernatant liquor to drain away from the oxide. At the Poplar Station a purifier 20 feet square was used to treat $3\frac{1}{2}$ million cubic feet of gas, one layer of oxide 24 inches deep being sufficient to remove all the cyanogen from this quantity of gas.

In this process from 10 to 15 per cent of hydrogen sulphide and from 15 to 20 per cent of ammonia contained in the gas are removed in the cyanide vessel, these quantities of course varying with the amount of cyanogen in the gas. The ammonium sulphocyanide recovered is between 3 and 5 pounds per ton of coal, dependent upon the method and temperature of carbonization, while the resultant liquor contains about 2.75 pounds of ammonium sulphocyanide per gallon, or about 26 per cent.

Before leaving the subject of sulphocyanides, it is of importance that the conversion of these cyanides into ammonia be taken up, and, as stated before, the Carpenter process as well as the liming process seem to give promise of the best results in this direction. The patented process of Mr. Charles Carpenter has not been explained in detail, but it is claimed it has been worked with "extremely satisfactory yields, and appears to be peculiarily adapted to all gas works and coke ovens which work up their own sulphate of ammonia."

This process differs from the earlier attempts of Burgevin and Burkheiser, and it appears to consist essentially of treating the sulphocyanide with an excess of sulphuric acid at some definite temperature, when ammonia, carbon oxysulphide, and acid sulphate of ammonia result.

According to the equation

$$KCNS + H_2SO_4 = HCNS + KHSO_4$$

the action of sulphuric acid upon potassium sulphocyanide will produce sulphocyanic acid, and if the latter is decomposed by water in the presence of an excess of sulphuric acid, ammonia and carbon oxysulphide will result, or

$$HCNS + H_2O = NH_3 + COS.$$

These two reactions will be very similar in the case of ammonium sulphocyanide, ammonium bisulphate resulting in the first place, or

$$NH_4SCN + H_2SO_4 = HCNS + NH_4HSO_4,$$

and the second reaction, or

$$HCNS + H_2O = NH_3 + COS,$$

will again give ammonia.

This process will depend greatly upon a proper working temperature, as if the temperature should be too high the cyanogen would possibly be volatilized and in consequence lost as sulphocyanic acid. It is stated,[1] however, that, working under proper conditions, a conversion of 98 per cent of the total nitrogen into ammonia should be possible. In addition to evolving carbon oxysulphide, it is very probable that some hydrogen sulphide will also result from the reaction, this being possibly due to the fact that carbon oxysulphide is readily absorbed by ammonia, which on evaporation will yield hydrogen sulphide. It is also possible that a portion of the carbon oxysulphide, in the presence of water and steam, might split up and yield carbon dioxide and hydrogen sulphide, or

$$COS + H_2O = CO_2 + H_2S.$$

Great attention has been aroused by the application of this process, and definite commercial results are therefore awaited with interest.

The second recent method of conversion, or the Lime method, is based on the lines laid down by Burgevin, and is applicable to such cases where calcium sulphocyanides are made. The calcium sulphocyanide is first evaporated to dryness, then mixed with an excess of slaked lime, and finally subjected to a heat of not less than 1000° F. The cyanides, in the presence of steam, are broken up under this temperature, and yield ammonia and carbon oxysulphide. The ammonia may be drawn off to an absorption vessel containing sulphuric acid, while the calcium oxysulphide will be in great measure removed by the excess of lime. It is stated that the manner in which the lime and cyanide are admixed is of great importance for the proper operation of the process.

The principal reactions are about as follows:

$$Ca(CNS)_2 + Ca(OH)_2 + 2H_2O =$$
$$2NH_3 + COS + CaCO_3 + CaS.$$

[1] "Jnl. of Gas Lighting." May 5, 1914.

The carbon oxysulphide thus formed is removed through a layer of lime 2 or 3 inches thick, this lime being placed over the mixture in the heating chamber. The reaction covering the removal of the carbon oxysulphide will then be

$$COS + 2Ca(OH)_2 = CaS + CaCO_3 + 2H_2O.$$

It is very essential that the carbon oxysulphide be removed in this manner, as otherwise it might combine with the ammonia and form urea, according to

$$COS + 2NH_3 = H_2S + CO(NH_2)_2.$$

It is claimed that this process will also give a conversion of 98 per cent, but the application of either method will of course depend upon local operating conditions.

The two systems of cyanogen recovery which have met with the most pronounced success on the European Continent and here, are that of Bueb and the one devised by Feld, the former making an insoluble ferrocyanide cake, and the latter a soluble cyanide sludge.

THE BUEB PROCESS

In the Bueb process iron sulphate, or copperas, and ammonia are used as the two reagents necessary to combine with the cyanogen, and a certain portion of the ammonia thus removed from the gas remains in the cyanide cake, the final resulting compound being ammonium ferro-ferro-cyanide.

The plant required for the extraction of cyanogen and the production of the cyanide cake is shown in Fig. 14, the various apparatus being enumerated from 1 to 22, and the method of operation is as follows:

Iron sulphate is stored in a bin, and the amount necessary for producing the requisite copperas solution is admitted into tank (2), where it is mixed with fresh warm water, or wash water from the filter press (10), the solution being agitated by means of the mechanically driven stirring arrangement in tank (2). The amount of iron sulphate ($FeSO_4$) required in the solution can be determined exactly after the cyanogen content of the gas is known, but during very warm weather a further amount of $FeSO_4$ is required to take care of the condensation from the gas, and thus to prevent a dilution of the liquor by the addition of water.

The copperas solution ($FeSO_4.7H_2O$) is pumped by pump (3) into the overhead supply tank (4), from whence a regulated quantity, depending on the strength of the solution, is permitted to flow into the top of the washer (5); the resultant liquor is permitted to remain in the washer until the copperas solution is saturated, after which it is run into the storage tank (6).

From the storage tank the sludge is pumped through the still (12), where a portion of the free ammonia is boiled off and condensed in the condenser (13), the sludge then passing to the neutralizing tank (7); this latter tank is lead-lined and hooded, and is provided with a steam coil as well as an agitator. A small quantity of sulphuric acid (oil of vitriol) is added to the sludge in this tank in order to neutralize it while the sludge is being heated to about 200° F., the acid being diluted with about three times its volume of water. The hydrogen sulphide liberated during the neutralizing period is caught under the hood of the tank and withdrawn through a pipe by means of a fan and conducted to a convenient boiler stack.

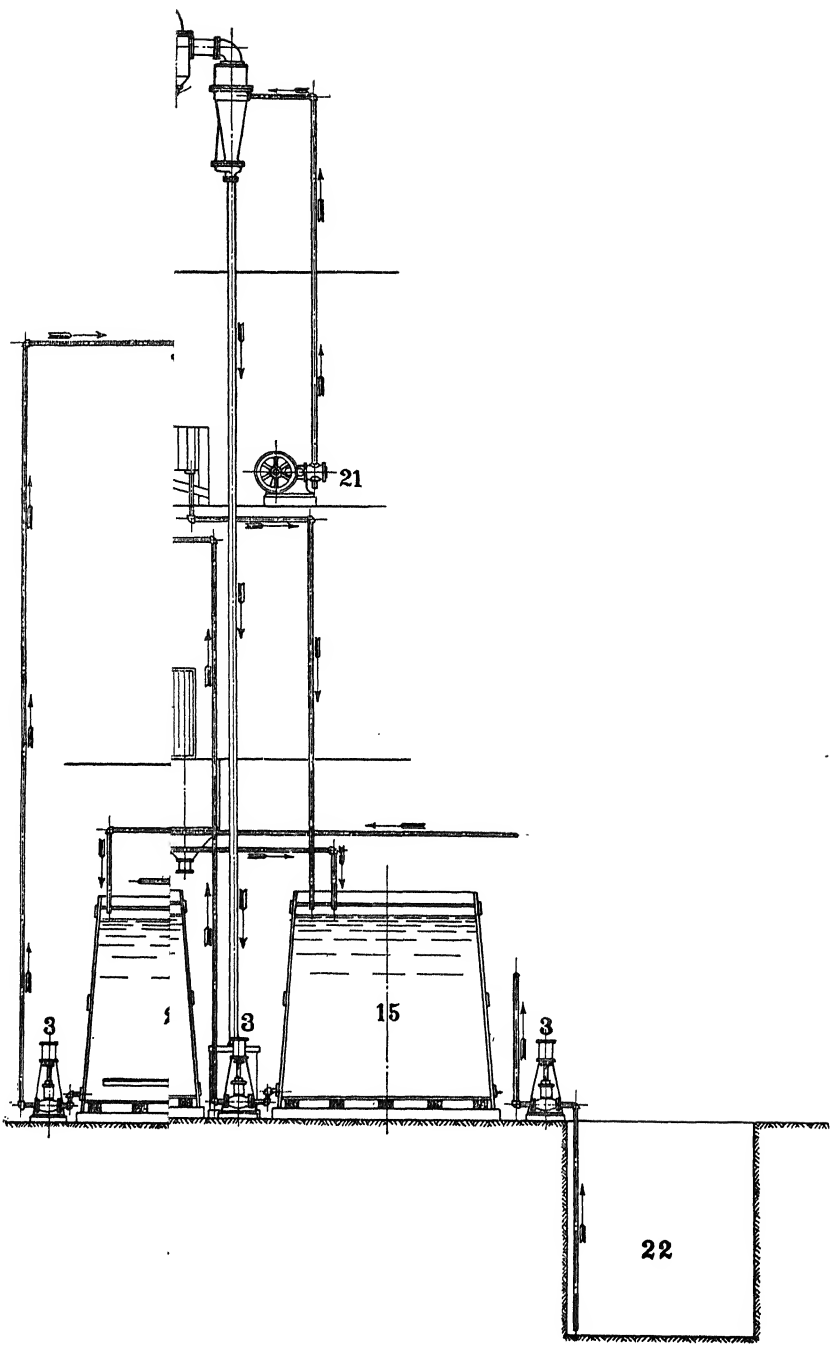
After neutralization the sludge is an insoluble double ferrocyanide of ammonium and iron, plus a solution of ammonium sulphate, a little ferrous sulphate, and a trace of free acid, and it is now run into the neutralized liquor storage tank (9), and is pumped from here to the filter press (10).

The sludge is pressed into a cake in the press, and after being washed is ready for the market, while the ammonium sulphate solution from the press is run into the precipitating tank (14), where it meets the concentrated ammonia, or ammonium sulphide from the condenser (13), this ammonia precipitating any iron which might be carried in the solution, thus preventing the discoloration of the resultant salts.

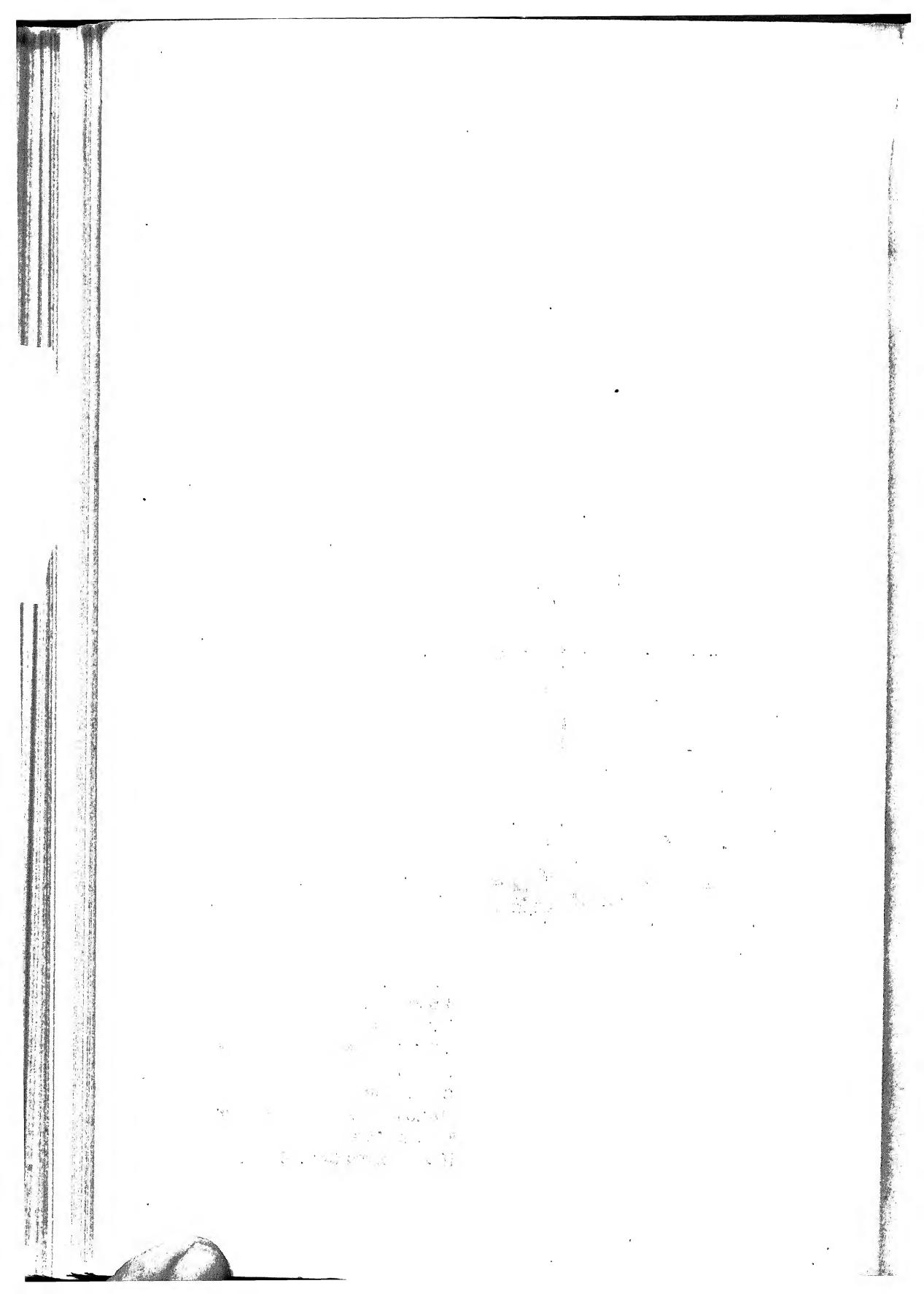
The sulphate solution is then pumped into the vacuum evaporator (16), where it is boiled to the point of crystallization, after which the crystals are dried in the centrifugal (19) and rotary dryer (20).

Chemistry of the Process:

The following reaction takes place in the upper section of the washer, where the $FeSO_4$ is precipitated and FeS, or iron sulphide, is formed, or



(*Facing Page 74*)



Reaction I:

$$2FeSO_4.7H_2O + 2H_2S + 4NH_3 = 2FeS + 2(NH_4)_2SO_4.$$

The next reaction takes place in the lower portions of the washer, where the CN reacts or combines with the FeS, or
Reaction II:

$$2FeS + 2NH_3 + 6HCN = (NH_4)_2Fe_2(CN)_6 + 2H_2S.$$

Due to the contact between the $(NH_4)_2Fe_2(CN)_6$ and the NH_3 and H_2S in the gas, a partial decomposition of the former takes place, resulting in the formation of some soluble $(NH_4)_4Fe(CN)_6$, or ammonium ferro-cyanide, or
Reaction III:

$$(NH_4)_2Fe_2(CN)_6 + H_2S + 2NH_3 = (NH_4)_4Fe(CN)_6 + FeS.$$

The next reaction takes place in the still, or
Reaction IV:

$$(NH_4)_4Fe(CN)_6 + FeS + \triangle = (NH_4)_2Fe_2(CN)_6 + (NH_4)_2S,$$

the resultant ammonium sulphide being found in the condenser.

The fifth reaction occurs in the neutralizing tank, where the sulphuric acid is added, or
Reaction V:

$$(NH_4)_4Fe(CN)_6 + FeS + H_2SO_4 = (NH_4)_2Fe_2(CN)_6 + (NH_4)_2SO_4 + H_2S,$$

and the last reaction takes place in the sulphate liquor precipitation tank, where the iron is precipitated from the liquor through the agency of the $(NH_4)_2S$ produced in the still and condenser, or
Reaction VI:

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4.$$

The salable product in this case is an insoluble ammonium ferro-ferro-cyanide cake and ammonium sulphate.

Assuming the carbonization of 300 tons of coal per day, and a cyanogen content of 120 grains per 100 cubic feet of gas, allowing 10,000 cubic feet of gas to the ton of coal, the estimated net revenue due to the extraction of cyanogen and the production of a cyanide cake, as well as ammonium sulphate from the press liquor, based on yellow prussiate of potash having a value of sixteen cents per pound, will be given by the following:

Cyanogen removed per day	514 pounds
$FeSO_4$ required per day	1845 "
Ammonia removed per day	345 "
Sulphate made per day	770 "
NH_3 in press cake per day	119 "
Sulphuric acid required per day	270 "

GROSS INCOME

Cyanogen[1]	514 pounds	at 13.25¢	= $68.10
Sulphate	770 "	at 3.00¢	= 23.10
Press Cake NH_3	119 "	at 7.00¢	= 8.33
Total gross income per day			$99.53

OPERATING EXPENSE

$FeSO_4$ per day	0.923 ton	at $ 9.50	= $ 8.77
Sulphuric acid	0.135 ton	at 11.50	= 1.55
Steam for neutralizer } Steam for evaporator }			= 3.00
Power, 870 K.W.H.		at 1¢	= 8.70
Labor			= 12.00
Miscellaneous supplies			= 4.00
Total operating expenses per day			$38.02
Net daily income			$61.51

In a series of eight tests made on a plant such as described here, the average result was as follows:

Cyanogen extracted from the gas	95.59%
Cyanogen recovered and fixed	98.93%
Ammonium sulphate recovered	95.76%

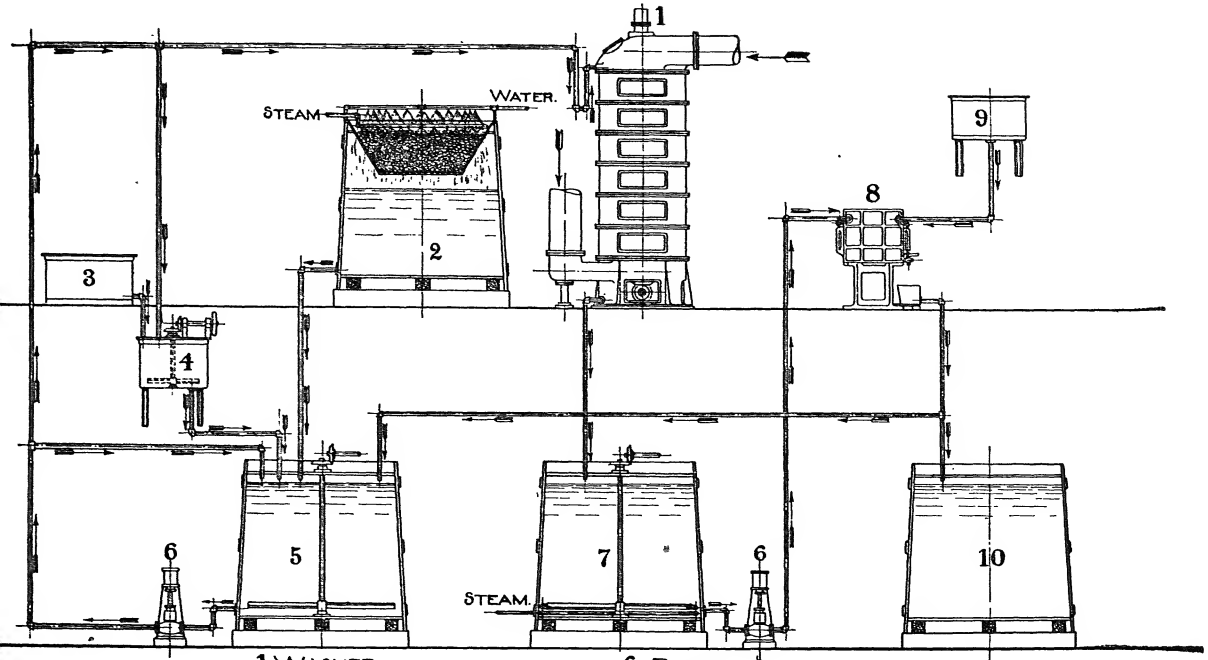
THE FELD PROCESS

A diagram of the Feld cyanogen-extracting process is shown in Fig. 15, and the operation proceeds as follows:

Lime is slaked in the vessel marked (3), the resultant CaO being mixed with water in (4), or in place of fresh water the unfiltered wash liquor from the wash-liquor tank (5) may be used. A concentrated solution of copperas, $FeSO_4.7H_2O$, is made in tank (2) by dissolving the iron sulphate with steam and water. The milk of lime in conjunction with the copperas solution is run into tank (5), this latter tank also being provided with an agitator, and the mixed solution thus formed is pumped into the top of the washer. The valve on the liquor inlet pipe is provided with a regulator so as to govern the exact quantity of washing medium admitted into the washer, thus insuring a saturated liquor at the overflow.

The resultant sludge is run from the overflow into tank (7); when this tank is almost full some fresh milk of lime is added, after which the liquor is thoroughly boiled, tank (7) being supplied with a steam coil for this purpose; care should be taken to keep the agitator in motion during this boiling

[1] The price given for cyanogen was prevalent prior to 1915; it has sold for as much as 85 cents per pound since then.



1 WASHER.
2 COPPERAS MIXER.
3 LIME SLAKER.
4 MILK OF LIME TANK.
5 WASH LIQUOR TANK.
6 PUMPS.
7 SLUDGE TANK.
8 FILTER PPRESS.
9 HOT WATER TANK.
10 CYANIDE LIQUOR TANK.

Fig. 15. — Feld Cyanogen Plant.

period. The liquor is now pumped into the filter press (8), the clear liquor coming from the press being divided in its flow, 75 per cent going to the storage tank (10), and 25 per cent to the wash-liquor tank (5). The press is washed out with hot water coming from the tank (9), this wash water flowing from the press to tank (10).

The product is calcium ferro-cyanide, and it can be shipped in tank cars or in barrels; it may also be concentrated by boiling if desired, thus reducing its shipping volume. If the liquor should be permitted to stand in storage for any protracted time, some milk of lime should be added from time to time in order to keep it alkaline.

Chemistry of the Process:

In order to explain the practical chemistry of this process, a plant producing 3,500,000 cubic feet of gas per day will be taken as an example under the following premises:

1 cubic meter of gas = 35 cubic feet.
1000 cubic feet of gas = 28.3 cubic meters.
1 gramme = 15.43 grains.
1 grain = 0.0648 gramme.

It is also assumed that the gas contains 120 grains of cyanogen per 100 cubic feet, or 77.75 grammes per 28.3 cubic meters, therefore one cubic meter will contain 2.75 grammes of cyanogen.

The reactions are as follows:

Reaction I:

$$FeSO_4.7H_2O + Ca(OH)_2 = Fe(OH)_2 + CaSO_4.2H_2O + 5H_2O.$$

Reaction II:

$$Fe(OH)_2 + 2Ca(OH)_2 + 6HCN = Ca_2Fe(CN)_6 + 6H_2O,$$

and by adding reactions I and II together we have

Reaction III:

$$FeSO_4.7H_2O + 3CaO + 6HCN = Ca_2Fe(CN)_6 + CaSO_4.2H_2O + 8H_2O$$

for which the molecular weights are

$$278 + 168 + 162 = 292 + 172 + 144,$$

and in order to maintain the constituents of the washing medium in excess of the theoretical quantities required by the HCN, we would make these molecular weights

$$300 + 200 + 150 = 250 + 220.$$

Under the above premises 55 cubic meters of gas would contain 150 grammes of HCN, and for 1000 cubic meters of gas we would require $\frac{1000}{55}$ = 18 times the above constants, or

$18\times 300 = 5400$ grammes of $FeSO_4.7H_2O$
$18\times 200 = 3600$ " " CaO
$18\times 150 = 2700$ " " HCN
$18\times 250 = 4500$ " " $Ca_2Fe(CN)_6$
$18\times 220 = 4000$ " " $CaSO_4.2H_2O_3$

besides some $CaCO_3$ and FeS.

Therefore for 100,000 cubic meters, or 3,500,000 cubic feet of gas in 24 hours, we would have:

560 kg. = 1232 pounds of $FeSO_4.7H_2O$, equivalent to
2000 liters = 500 gallons of iron sulphate liquor of 28 per cent strength.
360 kg. =792 pounds of lime, CaO, equivalent to
1100 liters = 275 gallons of milk of lime of 30 per cent CaO.
270 kg. = 594 pounds of HCN.
450 kg. = 990 pounds of $Ca_2Fe(CN)_6$, equivalent to
3000 liters = 750 gallons of calcium ferro-cyanide liquor of 15 per cent $Ca_2Fe(CN)_6$;

but as about one cubic meter of the liquor would be used daily to thin out the iron sulphate solution, it is necessary to filter 4000 liters, or about 1000 gallons of calcium ferro-cyanide liquor of 15 per cent strength; we also have 400 kg. = 880 pounds of $CaSO_4.2H_2O$, equivalent to 800 kg. = 1760 pounds of filter press cake containing 50 per cent H_2O.

The relative mixtures given above are only approximate; the greater the amount of filtered cyanide liquor which is mixed with the dissolved iron sulphate, the more concentrated will be the resultant calcium ferro-cyanide liquor. In Hamburg, Germany, a 15 per cent solution is used, but it is possible to work with from 18 to 20 per cent if the concentration of the $FeSO_4.7H_2O$ liquor is increased to 35 per cent, and then mixed with 1.5 cubic meters of filter liquor. It is also

permissible to mix the liquor with non-filtered calcium ferro-cyanide liquor; it is, however, better practice to only partly mix with unfiltered liquor, or on the other hand to entirely use filtered liquor in order to prevent the wash liquor becoming too thick.

The product coming from either the Bueb or Feld plant, is usually worked up into potassium ferro-cyanide, and in this case the working up of the sludge produced by the Bueb system requires additional apparatus for the removal and concentration of the ammonia carried in the sludge, while the working up of Feld sludge obviates the necessity of this ammonia apparatus, as the Feld system embraces the removal of cyanogen from the gas after the ammonia has been extracted.

Another system of cyanogen extraction, and one which is used in Great Britain, is that of Davis-Neill, in which the cyanogen is removed from the gas by washing with a solution of soda and ferrous carbonate, washers of the "Standard" horizontal or vertical type being used for this purpose. The resultant cyanogen liquor coming from the washers is run into a still, where the ammonia carried by the water is distilled off, the ammonia vapors thus produced being condensed and then run to the ammonia cisterns.

After being freed of ammonia, the cyanide liquor is pumped into a filter press, where the insoluble matter is separated and retained, the clear solution, as well as the wash water, from the press being then conducted into an evaporator, where the liquors are concentrated, after which they are run into crystallizing vats. These crude crystals, either sodium ferro-cyanide, or prussiate of soda, are now washed with mother liquor from the evaporator in order to remove excess soda and any insoluble matter, after which they are dissolved by means of hot water, no more water being used than is absolutely necessary to produce the required solution.

Insoluble matter carried in the crystals is then allowed to settle, after which the clear liquor is run into another set of vats, where the final crystals are formed on strings suspended in the liquid.

The wash liquor, consisting of soda and ferrous sulphate in solution, is prepared in mixing vats, and the precipitated ferrous carbonate is separated from the sodium sulphate solution in filter-presses, after which it is mixed with soda and water.

THE MANUFACTURE OF POTASSIUM FERRO-CYANIDE

A diagram showing a plant arranged for the manufacture of potassium ferro-cyanide or yellow prussiate of potash, using Bueb sludge, is shown in Fig. 16.

Bueb Sludge Plant:

The $(NH_4)_2Fe_2(CN)_6$ coming from the cyanogen washers is stored in tank (1), from whence it is transferred by pump (2) into the neutralizing vessel (3); here the sludge is neutralized with a small amount of sulphuric acid (oil of vitriol), as is done in the Bueb cyanogen extraction system, the acid being fed in small quantities from the overhead supply tank (4), this latter tank receiving its supply from the sulphuric acid storage tank (5), the delivery being effected by means of compressed air. After the sludge has been neutralized it is delivered by pump (6) to the storage tank (7).

By means of pump (8) the sludge is now transferred to the digester (9), where it is boiled with steam, the issuing vapors being condensed in the condenser (10) and collected in tank (11) as concentrated ammonia.

The boiled sludge is then run into the monteju (12), and is forced from thence by means of compressed air into the filter press (13); the ammonium sulphate liquor from the filter press flows into the settling boxes (14), and from thence into the sulphate liquor storage tank (15), and from here the clarified sulphate solution is transferred by pump (16) into the vacuum evaporator (17), where it is evaporated to crystallization.

The screw conveyor (18) carries the crystalline mash to the centrifugal (19), the mother liquor from the centrifugal returning to tank (15), while the salts are dried in the dryer (20). The "blue" cake left in the filter press (13) is carried by the conveyor (21) to the cake storage (22), and from thence over the cake chutes (23) to the disintegrators (24). Here the "blue" cake is broken up and mixed with a weak ferro-cyanide wash liquor and then run into the decomposer (25), where it is boiled with lime from the agitator (26), potash also being added at this point, until all of the ammonia is driven off.

The vapors from the decomposer (25) are condensed in

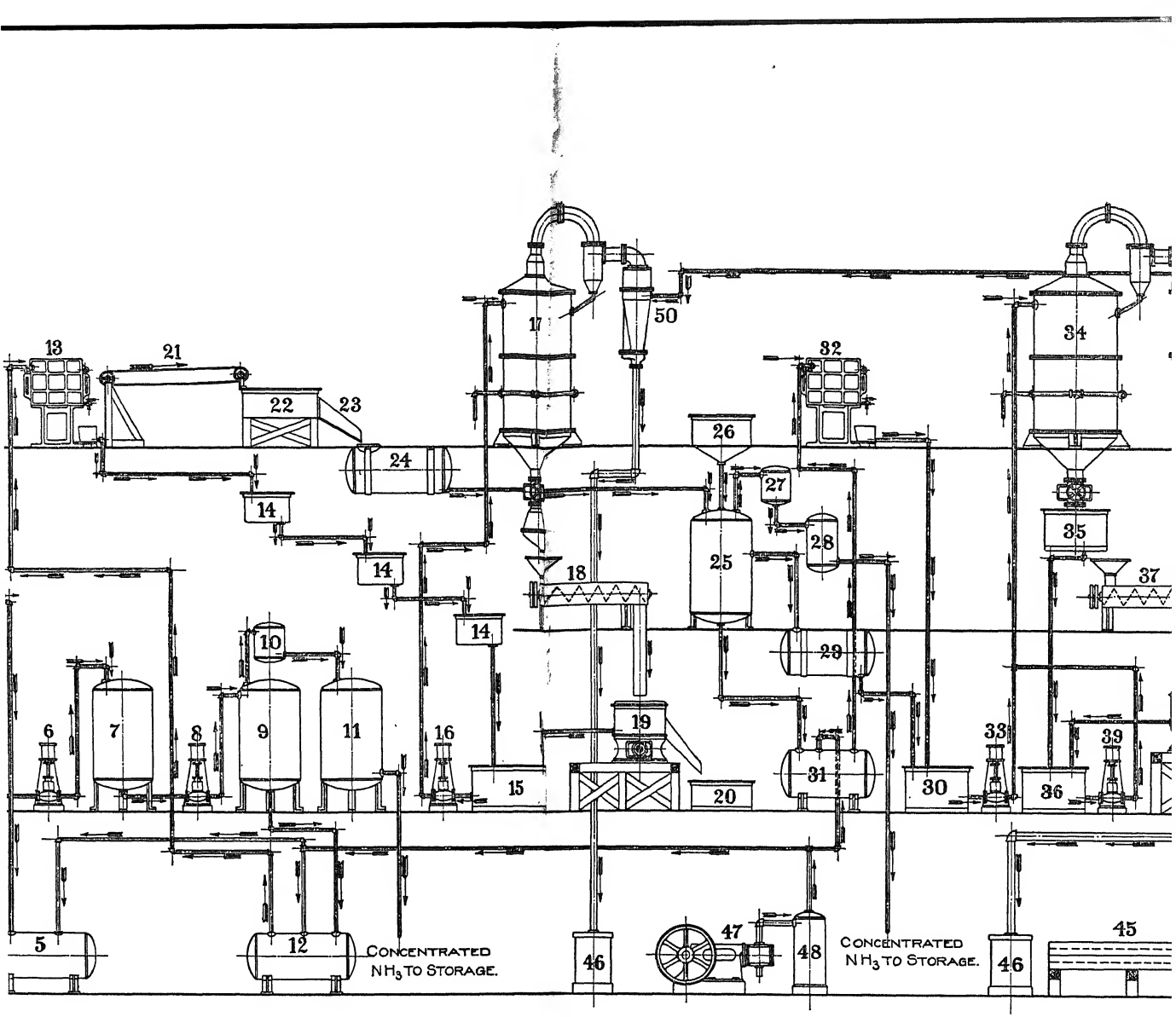
(27) and collected in the ammonia receiver (28) as concentrated ammonia. After being boiled, the ammonia free mash is allowed to settle in the decomposer, after which the clear liquor is drawn off into tank (29), and from there into the collector (30), while the mash is run into the monteju (31) and forced from there by compressed air into the filter press (32).

From this filter press all of the ferro-cyanide, in the form of potassium ferro-cyanide liquor, flows to the collector (30), while the press cake removed from the filter is principally iron. This weak potassium ferro-cyanide liquor is transferred by means of pump (33) from the collector to the vacuum evaporator (34), where it is evaporated to the point of crystallization, and then run into the salt cooler (35); here, while cooling, the greater portion of the potassium ferro-cyanide solidifies to a crystal mass which, after drawing off the mother liquor into tank (36), is transferred by the screw conveyor (37) to the centrifugal (38), the mother liquor from the centrifugals also being collected in tank (36). All of the mother liquor is finally transferred by means of pump (39) to the vacuum evaporator (34).

The crude salt is now dissolved in the dissolver (41), and the resultant solution is run into the concentrator (42), where the solution is again evaporated to the point of crystallization and the pure concentrated potassium ferro-cyanide liquor, ready to crystallize, is run while still hot into the crystallizer (43). After being completely cooled here, the potassium ferro-cyanide crystals deposit on the sides of the crystallizer and upon strings suspended in it; after drawing off the mother liquor and returning it to the concentrator (42) by means of pump (44), the crystals are removed to the dryer (45), and are then packed ready for shipment.

Yellow prussiate of potash, or potassium ferro-cyanide, $K_4Fe(CN)_6.3H_2O$, has a specific gravity of 1.8533, and its molecular weight is 422.36, made up by

Potassium,	K,	$= 39.10 \times 4 =$		156.40
Iron,	Fe,	$= 55.85 \times 1 =$		55.85
Cyanogen,	CN,	$= 26.01 \times 6 =$		156.06
Water,	H_2O,	$= 18.016 \times 3 =$		54.05
				422.36



RAGE.

11 CONCENTRATED AMMONIA TANK.
12 MONTEJU.
13 FILTER PRESS.
14 SETTLING BOXES.
GE. 15 SULPHATE LIQUOR STORAGE.
JMP. 16 SULPHATE LIQUOR PUMP.
TORAGE. 17 VACUUM EVAPORATOR.
18 SULPHATE CONVEYOR.
19 SULPHATE CENTRIFUGAL.
20 SULPHATE DRYER.

21 CAKE CONVEYER.
22 CAKE STORAGE.
23 CAKE SHTES.
24 DESINTEGRATORS
25 DECOMPER.
26 LIME AGITOR.
27 CONDENR.
28 AMMONI RECEIVER.
29 CLEAR LIQUOR TANK.
30 COLLECING TANK.

31 MONTEJU.
32 FILTER PRESS.
33 CYANIDE LIQUOR PUMP.
34 VACUUM EVAPORATOR.
35 SALT COOLER.
36 MOTHER LIQUOR TANK.
37 CRYSTAL CONVEYR.
38 CRYSTAL CENTRIFUGAL.
39 MOTHER LIQUOR PUMP.
40 SALT RECEIVER.

41 SALT
42 SALT
43 CRYS
44 MOTH
45 CRYS
46 TAIL
47 AIR
48 AIR
49 VAC
50 CONI

FIG. 16.—POTASSIUM FERRO CYANIDE PLANT OPERATING WITH "BUEB" SLUDGE

In the Bueb process of cyanogen extraction, 1.95 pounds of "blue," or $(NH_4)_2Fe_2(CN)_6$, are produced for every pound of cyanogen extracted from the gas, and to produce $K_4Fe(CN)_6.3H_2O$ we must add $2K_2CO_3$, or two molecules of potassium carbonate to one of the "blue," the commercial compound known as "black salt" and containing K_2CO_3 being used for this purpose.

The molecular weight of K_2CO_3 is 138, and that of $(NH_4)_2Fe_2(CN)_6$ is 304, therefore each pound of "blue" will require

$$\frac{138 \times 2}{304} = 0.908 \text{ pound of } K_2CO_3.$$

As the commercial "black salt" only contains 75 per cent of K_2CO_3, we will require $\frac{0.908}{0.75} = 1.211$ pounds of black salt for each pound of "blue" produced.

The amount of lime, CaO, required is 1.65 pounds per pound of fixed ammonia contained in the sludge, or using a commercial article containing 95 per cent CaO, we will require 1.73 pounds of lime per pound of fixed ammonia.

The amount of iron sulphate or copperas required will be the same as mentioned in the Bueb cyanogen extraction process.

Feld Sludge Plant:

As stated before, the production of yellow prussiate of potash from insoluble sludge is a roundabout procedure and requires much more labor and apparatus, and leads to possibly more ammonia losses than if a soluble sludge were used. Making calcium ferro-cyanide, which is soluble, in the washer does away with extra filter presses, sulphuric acid, and removal of ammonia, and it also requires less steam and improves the final product; besides this, less copperas will be required in the extraction process.

A plant to produce potassium ferro-cyanide, or, if desired, sodium ferro-cyanide from soluble sludge is shown in Fig. 17. Here, as explained under the Feld cyanogen process, the alkali constituent of the gas, ammonia, is replaced by an external alkaline medium, and the first half of the operation proceeds as explained in the Feld extraction process.

The ferrous sulphate solution is mixed in a suitable vat or tank with the proper equivalent of the alkaline agent, principally milk of lime, $Ca(OH_2)$, in such proportion that the alkali is in excess prior to its conveyance to the washer, which in this instance is located subsequent to the apparatus for ammonia removal.

In contact with the counter-current of gas, the ferrous hydrate, $Fe(OH)_2$, is converted by the means of hydrogen sulphide, H_2S, into ferrous sulphide, FeS, which absorbs the cyanogen compounds, the presence of the calcium compounds causing the formation of calcium ferro-cyanide, $Ca_2Fe(CN)_6$; this reaction, already given under the extraction process, may also be expressed as

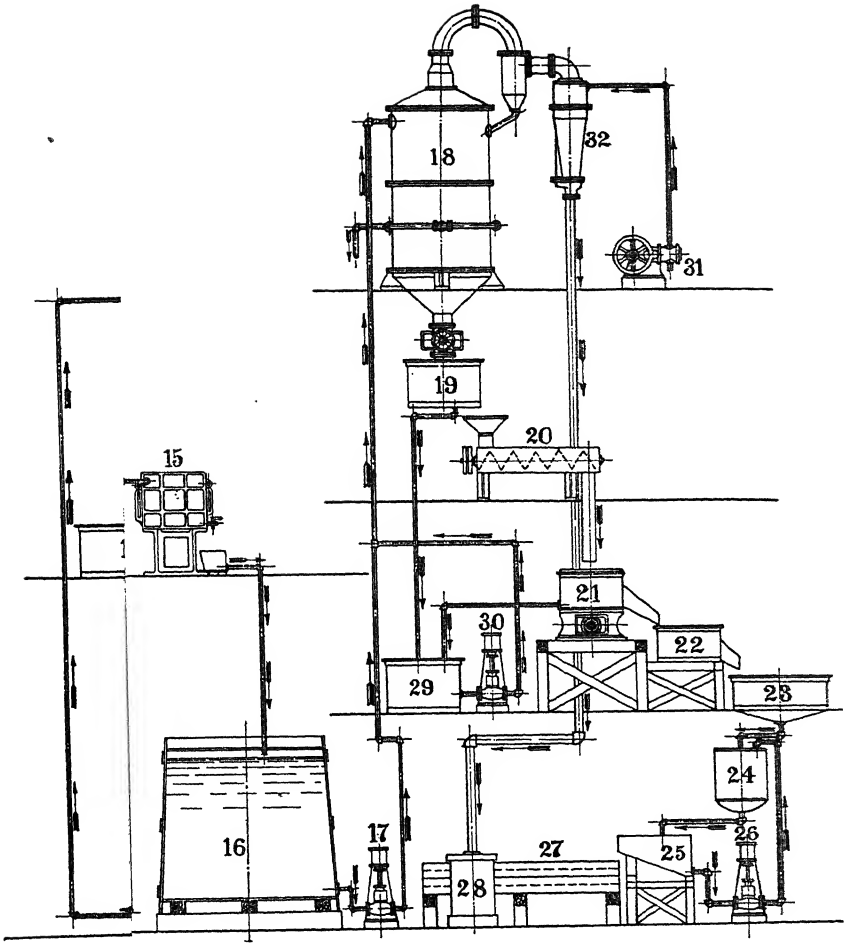
$$FeS + 2CaCO_3 + 6HCN = Ca_2Fe(CN)_6 + H_2S + 2CO_2 + 2H_2O.$$

The resultant sludge, a mixture of insoluble calcium sulphate, carbonate, etc., with traces of ferrous sulphide in a solution of calcium ferro-cyanide, is conveyed to a suitable vat or storage tank.

This liquid is filter-pressed and the clear calcium ferro-cyanide liquor is conveyed to a steam-heated digester, or still, in which, by the addition of alkaline potassium or sodium derivatives, principally carbonates, it decomposes, forming sodium or potassium ferro-cyanide and insoluble calcium carbonate, $CaCO_3$.

After separating the latter compound by means of filter pressing, the clarified ferro-cyanide solution is concentrated and the product purified by re-crystallization. The "slimes" or mud from the first filter press may be returned and mixed with the washing liquid, so proportioning the admixture as to prevent vitiation of its efficiency due to the presence of too large a proportion of an inactive agent.

Cyanogen from Spent Oxide. In plants not provided with a direct cyanogen-extraction system, the cyanogen-compounds will, to a great extent, be found in the spent oxide coming from the purifiers; the cyanogen content of this oxide makes the latter valuable, and although the oxide also contains sulphur varying from 30 to 50 per cent, the spent material in this country is rarely sold for its sulphur content, the cyanogen content being, as a rule, the basis on which the value is fixed.



RECEIVER.
DISSOLVER.
CONCENTRATOR.
ALIZER.
IER LIQUOR PUMP.
TAL DRYER.
IPE SEAL.
ER LIQUOR TANK.
ER LIQUOR PUMP.
JM PUMP.
ENSER.
LD" SLUDGE

(*Facing Page 84*)

The chemical works operating on spent oxide may prefer to remove the sulphur before attacking the cyanogen problem, but if this is not done, the sulphur must be carried through the entire process of cyanogen extraction; the latter method is, as a rule, the one usually pursued, because the removal of the sulphur is not only a difficult operation, and one requiring constant supervision, but it is also subject to a high fire risk and the action of the carbon disulphide used as the solvent is very injurious to the human system.

If the sulphur is to be removed, the spent oxide is ground to a fine powder and then placed within a cylindrical vessel having a perforated false bottom over which a filter cloth is spread to receive the oxide after the vessel has been filled nearly to the top, another filter cloth is placed over the top of the oxide, and the vessel closed tight. Carbon disulphide vapors from a steam-heated still are now charged into the closed vessel containing the spent oxide, the disulphide vapors condensing and passing down through the mass, relieving the latter of the sulphur burden during the passage, the liquor from the extracting vessel then being returned to the still. The apparatus is also provided with a condenser for taking care of any carbon disulphide vapors not condensed in the extractor, this condensed liquor being run to storage for charging the still when required.

When all sulphur has been removed from the oxide, the vapor connection to the extractor is closed off, and the carbon disulphide is driven off of the sulphur in the still, the resultant vapors being sent to the condenser and the carbon disulphide liquor from there to storage, after which it is again ready for the extraction process. The sulphur is now free of the solvent, and can be drawn off when melted, steam being blown through the residue in order completely to remove all traces of carbon disulphide

The sulphur thus obtained may be converted into sulphuric acid by roasting.

Quite a number of processes are in use for the extraction and conversion of the cyanogen compounds, but they are all based on three principals, viz.:

I. Lixiviation of the oxide for the removal of the soluble salts and the recovery of ammonia and sulphocyanides.

II. The conversion of the insoluble ferro-cyanides into sodium or calcium ferro-cyanides.

III. Conversion of sodium or calcium ferro-cyanide into potassium ferro-cyanide, if the latter is to be the end product.

Lixiviation is conducted in a series of filtering vats containing a false bottom of wooden beams, over which a layer of twigs is spread to a depth of about 4 inches, the top of the twigs being covered with a filter-cloth. Each vat communicates by means of a trough with at least three receivers. The vats are now filled with the spent oxide, and water is run into vat No. 1, filling same to a point about one inch above the oxide.

After being allowed to stand for about 24 hours, the resultant liquor is drawn off into the first receiver, and pumped from there into vat No. 2, vat No. 1 being again filled with fresh water. After another 24 hours this process is repeated, the liquor from No. 2 vat going to the second receiver and that from No. 1 to the first. From the second receiver the liquor now goes to vat No. 3, and after the proper period of settlement this series of changes is repeated until the original water from No. 1 vat has passed through at least eight vats in series, after which the liquor contains its burden of ammonia. This ammonia liquor is pumped to a storage tank, and from there to a still where it is distilled with lime, and the ammonia is recovered. The liquor after distillation contains calcium sulphocyanide in solution.

The second process consists in converting the insoluble ferro-cyanides into soluble compounds, and this may be done in a digester, or in a series of filtering vats similar to those described above.

The digester is provided with a vertical shaft operating a stirring paddle, and after the solid material from the lixiviation vats has been dried and pulverized, it is mixed with soda and lime and then charged into the digester. The digester is heated with direct steam, and the mass is cooked under constant agitation, the sludge from the bottom of the digester being run into filter-presses where the solution is separated.

If the filter vats are used, the process is similar to that described for lixiviation, but the solutions will be of a higher degree of concentration than those secured from the digester.

It will now be necessary to precipitate the ferro-cyanides, and while the solution from the digester contains both ferro-cyanide of sodium and of calcium, the solution from the vats contains all of the ferro-cyanide in the shape of calcium ferro-

cyanide, because lime only was used in this mixture, while both lime and soda were used in the mixture placed in the digester. Both solutions contain some sulphocyanide of calcium and ammonia. The ferro-cyanides may be precipitated by means of iron salt, ammonium salts, or potassium chloride.

If iron salts are used ($FeCl_2$ or $FeSO_4$), the ferro-cyanides will be precipitated in the form of prussian blue, ferrous or ferric chloride being used if the solution contains calcium ferro-cyanide, while ferrous sulphate is used if the solution contains sodium ferro-cyanide.

Owing to the presence of free ammonia, the sulphides, which are always found in the solutions coming from the digester, are alkaline, and they are acidified in a special vat, after which they are allowed to stand in order that the sulphur may separate out. The clear liquor can now be decanted, and it will then be ready for precipitation with the iron salt. This latter operation is performed in wooden vats, the solution being constantly stirred while the iron is being added; when precipitation is complete the supernatant liquor is drawn off, the prussian blue is filter-pressed and then converted into potassium ferro-cyanide by treating with potash or potassium carbonate, if this is the end product desired.

If the precipitation is to be performed by means of ammoniacal salts, the operation should be conducted in such manner that the salt is produced in sufficient quantity at the time of precipitation, by using lixiviated solutions which carry ammonia in such quantity as to make its neutralization with hydrochloric acid necessary. In order to accomplish this, some unlixiviated material, plus lime, should be added to the lixiviated solution, this procedure giving the amount of ammonia required for the reaction.

This operation is conducted in a vat provided with means for agitating the solutions, hydrochloric acid being added until the acid reaction is complete. The mixture is then heated to about 175° F., after which the double salt, according to the reaction,

$$Ca_2Fe(CN)_6 + 2NH_4Cl = Ca(NH_4)_2Fe(CN)_6 + CaCl,$$

will separate out in the form of a white powder. When precipitation is completed, agitation is stopped, and the precipitate is allowed to settle, the clear liquor being drawn off and the

precipitate filter-pressed. Some of the double salt will remain in the mother liquor, and this can be precipitated as prussian blue by means of iron salts.

The double salt, $Ca(NH_4)_2Fe(CN)_6$, may now be treated with lime in an agitating vessel in order to secure pure calcium ferro-cyanide according to the reaction

$$Ca(NH_4)_2Fe(CN)_6 + CaO = Ca_2Fe(CN)_6 + 2NH_3 + H_2O,$$

and the calcium ferro-cyanide may then be converted into potassium ferro-cyanide by using potassium chloride to precipitate the double salt $CaK_2Fe(CN)_6$, and then converting this salt into potassium ferro-cyanide by boiling with potassium carbonate according to the reaction,

$$CaK_2Fe(CN)_6 + CO_3K_2 = K_4Fe(CN)_6 + CaCO_3.$$

If it is desired to make the conversion with potassium carbonate in the presence of lime, the reaction will be

$$Ca(NH_4)_2Fe(CN)_6 + 2CO_3K_2 + CaO = K_4Fe(CN)_6 + 2CaCO_3 + 2NH_3 + H_2O.$$

The potassium ferro-cyanide solution thus obtained is now concentrated to 30° Bé., and then allowed to crystallize out.

If potassium chloride is to be used as the precipitating medium, according to equation

$$Ca_2Fe(CN)_6 + 2KCl = CaK_2Fe\,(CN)_6 + CaCl_2,$$

the double salt thus formed will be found to be slightly soluble. The calcium ferro-cyanide solutions are concentrated to 25° Bé., and then admitted into a small digester provided with an agitator, the precipitation in this digester being performed at a temperature of 175° F. The potassium chloride, in crystalline form, is used in excess, and the double salt $CaK_2Fe(CN)_6$ will be precipitated in the form of a pale-yellow powder, being later separated by filtration or decantation, washed with water, and finally treated with potassium carbonate in order to obtain potassium ferro-cyanide, the reaction covering this conversion being

$$CaK_2Fe(CN)_6 + CO_3K_2 = CO_3Ca + K_4Fe(CN)_6.$$

The calcium sulphocyanides in the liquor from the first lixiviation will be found in the residual solutions coming from the ammonia still, and they may be precipitated by the use of a potassium or sodium salt, and recovered by concentration and crystallization.

CHAPTER IV

AMMONIA

Ammonia is a product derived from the destructive distillation of coal, and it results from the union of nitrogen with hydrogen, or $N_2 + 3H_2 = 2NH_3$; besides being one of the principal sources of revenue, the removal of ammonia from gas is necessary on account of its destructive influence on the brass and copper work of meters and gas-fittings; when burned with gas it gives off noxious fumes of oxides of nitrogen.

The usual method employed for the removal of ammonia depends upon its solubility in water, and at ordinary temperatures water can absorb about 708 times its volume of ammonia gas, the absorption increasing with a decrease in water temperature, or

One volume of water at 32° F. will absorb 1050 volumes of NH_3
One volume of water at 50° F. will absorb 813 volumes of NH_3
One volume of water at 59° F. will absorb 727 volumes of NH_3
One volume of water at 68° F. will absorb 654 volumes of NH_3
One volume of water at 77° F. will absorb 586 volumes of NH_3
One volume of water at 183° F. will absorb 180 volumes of NH_3

providing the pressure of the ammonia gas is equal to that of the atmosphere, and if the gas carries no tar burden.

If it is assumed that the amount of ammonia in crude gas is 2 per cent by volume, the ammonia will be capable of exerting only 2 per cent of the total pressure of the gas. It must also be remembered that the strength of a solution of ammonia in water is dependent upon the pressure of the ammonia gas with which it is in contact; therefore the strength of the resultant liquor will be dependent upon the pressure exerted by the ammonia in the crude gas coming in contact with the liquor.

Liquors of various strengths and temperatures have definite pressures, or tensions, and these pressures are capable of giving up ammonia to the gas if the ammonia pressure of the

gas is less than that of the liquor, but if the ammonia pressure of the gas is greater than that of the liquor, the liquor will be able to extract more ammonia and gain in strength until a point is reached at which the pressures in gas and liquor are equalized.

The usual gas-works method of operation as practised in America removes the ammonia by condensation and washing, the first portion of the ammonia being removed in the hydraulic main due to the condensation of water vapors, which thus absorb ammonia. Cooling the gas in the condensers also causes the deposition of quite an amount of water which in turn absorbs more ammonia, the final ammonia being removed in the scrubbers or mechanical washers, using as little wash water as is consistent with the result desired, viz., strong liquor. Table XII gives the strength, weight, etc., of ammonia liquors.

TABLE XII. — AMMONIA

Strength in oz.	Weight per gal.		Per cent of NH_3	Twaddle at 60° F.	Specific gravity water basis	Weight per gal. in lbs. at 60° F.
	oz.	lbs.				
0	0.000	0.0000	0.0000	0.00	1.0000	8.3328
1	0.347	0.0217	0.2591	0.50	1.0025	8.3560
2	0.689	0.0434	0.5182	1.00	1.0050	8.3770
4	1.388	0.0868	1.0364	2.00	1.0100	8.4180
6	2.082	0.1301	1.5546	3.00	1.0150	8.4600
8	2.786	0.1735	2.0728	4.00	1.0200	8.5020
10	3.469	0.2169	2.5910	5.00	1.0250	8.5440
24	8.328	0.5205	6.2184	12.00	1.0600	8.8350
28	9.726	0.6079	7.2548	14.00	1.0700	8.9180
32	11.104	0.6840	8.2912	16.00	1.0800	9.0020
36	12.492	0.7807	9.3276	18.00	1.0900	9.0850
40	13.878	0.8676	10.3640	20.00	1.1000	9.1680
44	15.265	0.9544	11.4004	22.00	1.1100	9.2530
48	16.654	1.0411	12.4368	24.00	1.1200	9.3360
52	18.041	1.1276	13.4732	26.00	1.1300	9.4200
56	19.429	1.2143	14.5096	28.00	1.1400	9.5030
60	20.816	1.3014	15.5460	30.00	1.1500	9.5860
70	24.286	1.5179	18.1370	35.00	1.1750	9.7950
80	27.755	1.7352	20.7280	40.00	1.2000	10.0040

This table is to be used in connection with the "saturation" test with H_2SO_4, used as a check on scrubber operation as performed in many gas works, and is not indicative of the total NH_3 content of the liquor, as only free NH_3 will combine with the acid. The "ounce strength" in col. 1 means the ounces of H_2SO_4 that will neutralize one gallon of the liquor used, and the other data is a measure of the NH_3 equivalent of the acid used for neutralization.

In order to determine the total NH_3 content of the liquor, it is necessary to distill in the presence of an alkali, such as caustic soda or hydrated lime, and catch the vapors in a measured quantity of normal H_2SO_4 solution, each c.c. of which is equivalent to 0.01703 gramme of NH_3. The excess acid is titrated with normal NAOH solution, and the calculation for per cent of NH_3 will be:

$$\frac{(\text{c.c. N/}_1\text{H}_2\text{SO}_4 - \text{c.c. N/}_1\text{NAOH})\ 0.0173}{\text{weight of sample}} = \text{per cent } NH_3, \text{ or}$$

$$\text{per cent } NH_3 \times 3.88 = \text{per cent } (NH_4)_2SO_4.$$

Assuming that the nitrogen in the coal amounts to 2 per cent, and that of this 15 per cent forms ammonia, the following example will illustrate how to calculate the amount of ammonia present in the raw gas, under the above conditions, also the amount of ten-ounce liquor to be expected provided all of the ammonia produced is recovered, also the amount of sulphate which this quantity of ammonia should produce.

As 2 per cent of the coal is assumed to be nitrogen, the amount present in one ton of coal will be 2000 lbs. $\times$ 0.02 = 40 pounds, and if 15 per cent of this nitrogen is converted into ammonia, we would have 40 $\times$ 0.15 = 6 pounds of nitrogen as ammonia per ton of coal, but as ammonia is a compound consisting of 14 parts of nitrogen and 3 parts of hydrogen, or if every 14 parts of nitrogen are equal to 17 parts of ammonia, we would have

$$\frac{6 \times 17}{14} = 7.28 \text{ pounds of ammonia,}$$

equivalent to

$$\frac{7.28 \times 7000}{100} = 509.6 \text{ grains per 100 cubic feet of gas.}$$

This amount of ammonia expressed in percentage by volume can be determined by multiplying the weight in grains of a cubic foot of hydrogen by half the molecular weight of ammonia, and dividing this product into the number of grains of ammonia per 100 cubic feet of gas, or we will have in this case

$$\frac{509.6}{37.15 \times 8.5} = 1.61 \text{ per cent.}$$

The ounce strength of liquor is based on the sulphate radical, or $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$, in which 34 parts of ammonia by weight require 98 parts of sulphuric acid, thus forming $34 + 98 = 132$ parts of ammonium sulphate. As the ton of coal produces 7.28 pounds of ammonia, we would have

$$\left(\frac{7.28 \times 98}{34}\right) 16 = 335.68 \text{ ounces.}$$

equivalent to 33.568 gallons of 10 ounce liquor.

The amount of sulphate produced by this amount of ammonia will be $7.28 \times 3.88 = 28.25$ pounds per ton of coal.

Raw ammonia liquor from the plant usually contains from 1 to 2 per cent of ammonia, and due to the cost of transportation it would not in most cases be economical to sell this liquor in its diluted state; the raw liquor is, therefore, usually worked up for one of the following ammonia products:

1. Concentrated liquor,
2. Aqua ammonia,
3. Sulphate of ammonia,

but the product to be recommended for any particular gas works must necessarily depend upon local market conditions.

Concentrated ammonia is a product in which the raw liquor has been freed of a large portion of water, and it is used for producing other ammonia products.

Aqua ammonia is a solution of ammonia in distilled water, a great deal of it, in a dilute solution, being used for cleansing purposes.

Ammonium sulphate is produced by distilling the liquor, and absorbing in sulphuric acid; by passing the gas through an acid bath, thus absorbing the ammonia, or by combining the ammonia in the gas directly with the sulphur radical, and subsequent oxidation, without the use of sulphuric acid.

Sulphate finds its greatest use in the manufacture of fertilizer, it being the nitrogen-carrying agent in this product. For this latter use, sulphate has lately found an active competitor in calcium cyanamide, a product of the electric furnace, where calcium carbide absorbs nitrogen from the atmosphere to form cyanamide with the liberation of carbon, this product containing from 14 to 22 per cent of nitrogen which is liberated as ammonia when treated with water, thus making it suitable for agricultural fertilizer. It appears that with soils which are not rich in humus or not deficient in lime, cyanamide is almost as good, presuming that they all have the same nitrogen content, as ammonium sulphate or sodium nitrate, but it is of doubtful value with peaty soils, or soils containing little lime, and it is not nearly as good as either of the above for a soil top-dressing.

Ammonium chloride (sal ammoniac) is obtained by using hydrochloric acid as an absorbing agent, followed by evaporation and crystallization. In the United States the principal source of sal ammoniac is ammonium sulphate, this compound being heated in conjunction with common salt. It is used as an agent in galvanizing iron, for soldering, and in electric batteries.

Liquid anhydrous ammonia is produced by freeing the ammonia gas of all moisture and impurities, after which it is liquefied by pressure; it is used for the production of low temperatures by the absorption of heat, as in refrigeration.

Ammonium carbonate is produced by heating a mixture of ammonium sulphate in conjunction with calcium carbonate, and it is used for scouring purposes, especially wool.

Ammonium nitrate is produced by neutralizing nitric acid with ammonia, and it is used in the manufacture of explosives.

There are many other ammonia compounds, but the ones mentioned above are the principal products, and they can all be prepared from ammonium sulphate, thus making this latter compound one of the principal by-products of coal distillation.

The crude liquor coming from the works contains ammonia in combination with various radicals, the principal ones of which are ammonium carbonate, sulphide, chloride, and sulphate. These salts may be grouped into two classes in accordance with their conduct during the process of boiling the crude liquor.

Carbonates of ammonia as well as sulphides of ammonia, below the boiling point of the liquor, decompose into carbonic acid, hydrogen sulphide, and ammonia, and as these are completely freed at the boiling point, they are classed as "free" ammonia compounds. On the other hand ammonia combined as chloride and sulphate can only be liberated by the addition of some stronger alkali, lime in the form of milk of lime being usually introduced into the solution for this purpose.

Analysis will give the amount of free and fixed ammonia in the liquor, from which the yield of ammonia as well as the amount of lime to be used can easily be deduced; as a rule the liquor contains from 70 to 80 per cent of free, and 20 to 30 per cent of fixed, ammonia.

The working up of the liquor is usually effected in continuous stills (Fig. 18), operating with a supply of live steam, and as the principle of design and operation is practically the same in the usual stills on the market, only one method will be described, the others differing only in detail, and not in principle.

The still usually consists of a series of superimposed sections, one mounted upon the other, constructed of cast iron, each section being provided with a steam passage in the bottom covered with a hood or bell, and an internal overflow for liquor. These sections should be liberally provided with cleaning holes, by means of which access can be had to every part of the interior, so that the apparatus can be thoroughly cleaned without dismantling it. The liquor, having been previously heated, enters at the top of the still and flows from section to section in a direction opposite to that of the steam, which enters at the bottom, passes up through the steam passages, and is caused to pass through the liquor by means of the hoods or bells.

The crude liquor is thus gradually brought to the boiling point, the free ammonia and other gases mixing with the steam in the upper portion of the apparatus. The milk of lime is introduced in small quantities into the lower, or liming sections, the hoods of these sections having a somewhat deeper seal than the others, in order to permit of more efficient mixing of lime and liquor. A final boiling of the liquor in the lower sections completely liberates all of the fixed ammonia, and the stills should be so operated that

the waste liquors leaving the bottom should not contain more than 0.005 per cent of ammonia.

Great precaution must be taken in the operation of the ammonia stills, as it is at this point where a large amount of the ammonia produced may be lost, due to improper or inefficient liming for the liberation of the fixed ammonia, the liming apparatus being the subject of a good deal of attention if proper pecuniary returns are expected, and, besides maintaining a constant flow of liquor to the stills, it is essential to see that a constant feed of milk of lime is secured, and that the gravity of the solution, or its alkali content, is constantly maintained at predetermined figures based upon the quantity of fixed ammonia in the liquor.

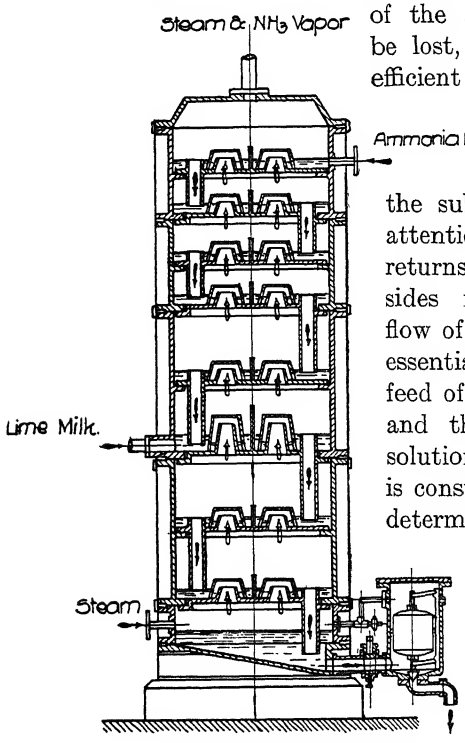


Fig. 18. — Ammonia Still.

Concentrated Ammonia: A plant for concentrating the liquor produced in the works is shown in Fig. 19, and it consists of a still, as described above, a reflux cooler, automatic waste lime overflow, lime washer, sectional cooler, collecting tank for the storage of concentrated liquor, automatic steam lime pump with agitator tank, iron hand pump and an overhead supply tank.

The crude liquor is delivered from the overhead supply tank (1) to the sectional cooler (2), where the vapors coming from the still are cooled, thus transferring their heat to the incoming crude liquor, and thereby reducing the amount of cooling water required. The crude liquor enters the bottom of the cooler, leaving it at the top, and passing from thence

to the upper portion of the still (3). As described above, the still consists of several lime and several water sections, the free ammonia being volatilized in the water sections.

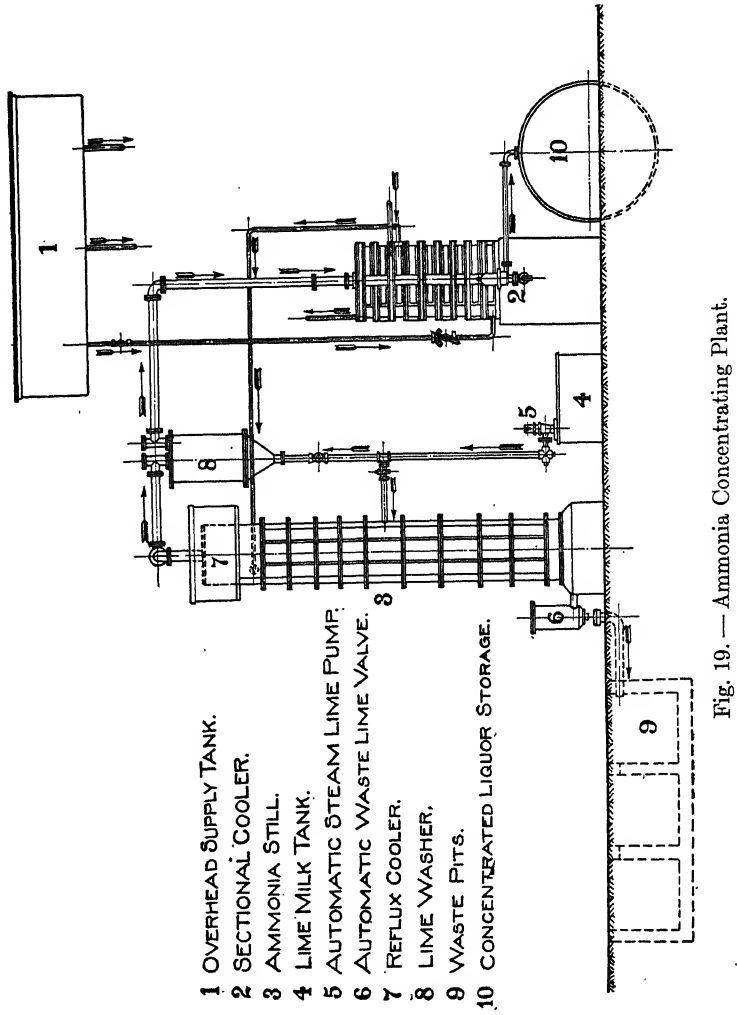


Fig. 19. — Ammonia Concentrating Plant.

The lime enters the upper liming section, being pumped from the agitator tank (4) by means of the automatic lime pump (5); this pump is so controlled by means of an air brake (compressed air being supplied by means of a small air pump

not shown) that the delivery of milk of lime can be varied within very wide limits, or from one to ten double strokes per minute. The lime milk is agitated in the tank by means of an attachment connected by a lever to the piston rod of the pump, thus ensuring a perfect mixture of lime and water.

In the first lime section the lime becomes thoroughly mixed with the liquor, being then passed through the remaining sections and leaving the still at the bottom through the automatic waste lime overflow. This overflow valve is mounted in the bottom of a cast-iron casing, a lead-covered sheet-iron float being connected to the valve by means of a stem. The float moves up and down inside the casing, and the steam pressure acting on it is the same as that in the lower part of the still, so that the water level at which the valve opens always remains constant.

The volatile ammonia is expelled through prolonged boiling of the liquor, but the fixed ammonia can only be expelled by decomposing the salts with lime. The vapors rise through the tubes in the bottoms of the sections, being baffled by means of the hoods or bells located over the tubes, while the raw liquor, as well as that portion of the liquid condensed by the cooling action of the air, gradually flows through the internal overflow tubes from one section to the other. The frequent repetition of this cycle in the different sections of the still produces ammonia vapors of high strength.

In the bottom section of the still the waste liquor is freed of practically the last traces of ammonia. The ammonia vapors are now cooled in the water-cooled top section of the still and they are then dephlegmated in the reflux cooler (7), thence passing into the lime washer (8), and are finally condensed in the sectional cooler (2). The reflux cooler is arranged over the still and can be fed with more or less water as required for the purpose of condensing a large amount of vapors and sending them back into the still in order to produce a concentrated liquor of high NH_3 content, and this liquor usually contains from 15 to 25 per cent of ammonia, dependent upon the manner of operating the plant.

As the formation of ammonium carbonate may obstruct the condenser, or sectional cooler, the vapors from the still

are first passed through the lime washer (8), in which sufficient lime should be injected to prevent any excessive formation of carbonate. The lime milk is injected into the washer by means of the automatic pump (5), the delivery pipe from this pump being provided with a proportional distributing valve system, so arranged that two successive strokes of the pump will deliver the lime milk into the still, and the following stroke will deliver to the lime washer. The lime milk from the washer in turn flows into the first liming section of the still, where it gives up the ammonia absorbed in the washer and mixes with the lime direct from the pump.

The sectional cooler (2) is made of cast iron, the upper portion of the cooler being supplied with the necessary amount of cooling water, this amount being considerably less than that used in the usual cooler, because the principal cooling medium consists of the crude ammonia liquor coming from the supply tank (1).

This entire process for producing concentrated liquor is practically automatic, it being only necessary to carefully attend to the filling of the crude liquor supply tank (1) so as to ensure a proper feed to the still, and to see that lime is delivered at proper fixed intervals.

Concentrating plants as erected and operated in America vary a great deal in detail, but the method of operation as given above will cover almost any system in use, as the principle of concentration is a fixed one.

The heating of the ammoniacal liquor, and bringing it up to the boiling point, requires the greater amount of steam used, the remainder of the steam being required for heating the water in the lime milk, for splitting up and expelling the ammonia, for replacing the amount of heat lost by radiation, and for supplying that portion condensed to carry the ammonia in solution.

Unger (John S. Unger, Chicago) gives the amount of steam required in his 30-inch still, having 186 square feet of radiating surface, radiating 200 B.T.U. per square foot per hour, with steam containing 960 B.T.U. per pound, as follows:

Steam required per pound of ammonia to concentrate a liquor containing 1 per cent of ammonia,

Item	B. T. U.	Steam lbs.	Per cent
One pound of ammonia requires for dissociation...	1,880	1.97	8.37
To heat 100 pounds of liquor from 70° to 220° F...	15,000	15.63	66.43
To heat 4.2 pounds water with the lime.....	630	0.66	2.80
Heat radiated in three minutes	1,860	1.94	8.25
Pounds of water in concentrate		3.33	14.15
Total steam required per lb. of NH_3 ..... or 1.96 lbs. of steam per gallon of liquor		23.53	100.00

Steam required per pound of ammonia to concentrate a liquor containing 2 per cent of ammonia,

Item	B. T. U.	Steam lbs.	Per cent
One pound of ammonia requires for dissociation..	1,880	1.97	13.35
To heat 50 lbs. of liquor from 70° to 220° F.	7,500	7.81	53.02
To heat 4.2 pounds water with lime	630	0.66	4.48
Heat radiated during one and one-half minutes...	930	0.97	6.58
Pounds of water in concentrate		3.33	22.57
Total steam required per pound of NH_3 ..... or 2.52 pounds of steam per gallon of liquor.		14.74	100.00

The above figures indicate that it requires eight and three-quarter pounds more steam, per pound of ammonia, to concentrate a 1 per cent liquor than is required with a 2 per cent liquor.

Lime Required:

One and sixty-five hundredths pounds of lime are theoretically required to replace one pound of ammonia, but as the usual commercial lime contains some impurities, this amount is usually increased to 2.5 pounds, which latter also allows for some excess. This lime is only required for the fixed ammonia, and if five pounds of ammonia containing 25 per cent of fixed salts should be recovered per ton of coal, we would require $(5 \times 0.25)\ 2.5 = 3.125$ pounds of lime per ton of coal.

Cooling Water:

About nine gallons of cooling water at a temperature of 60° F. are required as a maximum, but in well constructed and operated plants not more than seven gallons of water per pound of ammonia should be used.

EARNING CAPACITY OF A CONCENTRATING PLANT

In the following example a plant carbonizing 300 short tons of coal per day will be used as a basis, or one producing 12,000 gallons of 8 oz., or 2.0728 per cent liquor per day, which with 250 maximum working days will give 3,000,000 gallons of liquor per year, recovering 5 pounds of ammonia per ton of coal.

As we will assume that the plant is constructed as described above, where the crude liquor is preheated in the sectional cooler by means of the concentrate proper, only about 20 pounds of steam per pound of ammonia in a 1 per cent liquor, and about 12 pounds of steam in a 2 per cent liquor, will be required.

I. Labor:

300 operating days, 3 men at $2.00 per day	$1800.00
20 days cleaning waste pits, 1 man at $1.50	30.00
Total labor	$1830.00

II. Materials:

4500 M pounds of steam at 20 cents	$ 900.00
117 tons of lime at $8.50	994.50
2.75 million gallons of water at $10.00	27.50
Total materials	$1922.00

III. Miscellaneous:

Drayage on about 100 tons of sediment at 50¢	$ 50.00
Illuminating the plant	60.00
Estimated repairs	200.00
Lubricating oil, waste, etc.	150.00
Total Miscellaneous	$460.00

The total cost per year will then be:

I. Labor	$1830.00
II. Materials	1922.00
III. Miscellaneous	460.00
Total	$4212.00

making the total cost of concentrating one pound of ammonia, less interest and depreciation on plant, 1.123 cents, while the gross revenue at eight cents per pound will be

$$375000 \times \$0.08 = \$30,000.00,$$

giving a net revenue, less interest and depreciation, of

$$\$30,000.00 - \$4,212.00 = \$25,788.00 \text{ per year.}$$

If the weak liquor, as produced in the works, can be sold as such, and if the ammonia in this liquor based on the above price of concentrate is worth six cents a pound, the yearly gross revenue for this ammonia would be $22,500, but from this would have to be deducted the added freight due to shipping a larger bulk, if the ammonia liquor is to be transported away from the works, as well as pumping charges. In order to make the sale of weak liquor a profitable undertaking as compared with concentrate, it would be necessary that an ammonia works which would take the entire output of liquor be established in very close proximity to the gas-works.

Aqua Ammonia:

This plant, a diagram of which is shown in Fig. 20, consists of an ammonia still (3), provided with a reflux cooler (7); automatic lime overflow (6); lime washers (8); coolers (9), the latter consisting of wooden vats containing lead-cooling coils; overhead supply tank (1); liquor heater (2); lime tank (4); automatic lime pump (5); charcoal filters (10); oil washer (11); caustic soda washer (12); absorbers (13); and lime trap (14).

Chemically pure ammonia is a concentrated solution of caustic ammonia in water, and can be made directly from the gas liquor; it is a colorless, clear liquid and should not expel any empyreumatic odors, while a lead-paper test should show the entire absence of sulphides.

Aqua ammonia is stored in carboys or drums, neither of which should be filled to capacity, and they must be kept in a cool place to avoid bursting due to excessive gas pressure. If drums are used for storage or transportation, care should be taken to caulk them tightly in order to avoid loss of ammonia by evaporation.

The manufacture of aqua ammonia in some localities is very remunerative, as the demand for this product is very large in the textile industry as well as in refrigeration, but the plant is also at times subject to large losses.

The crude liquor from the supply tank (1) enters the heater (2) by gravity, the crude liquor being heated here through the medium of the waste liquors coming from the still; from the heater the liquor enters the top of the still (3), where it is treated with steam and lime as in the previous case. The offgoing vapors are cooled in the reflux cooler (7) and then enter into the lime washers (8), passing from one to the other, and from thence into the lime trap (14), the vapors being thus deprived of all lime water.

After leaving the trap the vapors enter the coolers (9), going from thence into the first charcoal filter (10), where the moisture is expelled, and then into the oil washer (11), where tarry matters are removed. The vapors are now passed through the remaining charcoal filters in order to expel all empyreumatic substances, and from thence into the caustic soda washer (12), this latter washer being filled with a 10 per cent solution of caustic soda for the purpose of arresting any sulphides which may be contained in the vapors, and the purified vapors then finally enter the saturators or absorbers (13).

This process of absorption produces heat, and the receivers of the absorbers are therefore kept cool by being placed in wooden vats filled with water.

THE EARNING CAPACITY OF AN AQUA AMMONIA PLANT

Capacity of plant at 300 tons of coal per day and 250 maximum working days, giving 3,000,000 gallons of liquor per year.

I. Labor:

300 operating days, 3 men at $2.00	$1800.00
20 days cleaning waste pits, 1 man at $1.50	30.00
300 days liming, cleaning drums, loading, etc., 4 men at $1.50	1800.00
Total labor	$3630.00

II. Materials:

17,500 M. pounds of steam at 20¢	$3500.00
450 tons of lime at $8.50	3825.00
1500 bushels of charcoal at 15¢	225.00
6 million gallons of water at $10.00	60.00
Total material	$7610.00

III. Miscellaneous:

12 gallon carboys, 12,500 at $1.60	$20,000.00
Drayage, 550 tons of sediment at 50¢	275.00
Illuminating the plant	65.00
Estimated repairs	750.00
Oil, waste, etc.	200.00
Total miscellaneous	$21,290.00

The total cost per year will then be:

I. Labor	$ 3,630.00
II. Materials	7,610.00
III. Miscellaneous	21,290.00
Total	$32,530.00

The gross revenue to be derived will amount to:
780 tons of Aqua of 26° Bé., equivalent to about 27.2% NH_3, at $102.00 ..... $79,560.00
and the net revenue will be $79,560.00 − $32,530.00 = $47,030.00 per year, less depreciation and interest. This revenue should be increased after the first year, because a number of the carboys will be returned to the plant, thus making their cost less than originally, only a nominal allowance being made to the purchaser for them.

INDIRECT SULPHATE PROCESS

This plant consists of an overhead supply tank (1); a liquor heater (2); ammonia still (3); lime agitating tank (4); automatic lime pump (5); automatic overflow (6); water trap or separator (7); saturators (8); acid catch box (9); and drainage table (10), all as shown in Fig. 21.

Here again, the principle of design remains the same, but the various manufacturers have subjected the various parts of the plant to variations complying with individual experience.

The liquor from the supply tank flows into the preheater, where it is heated by the escaping waste liquors before they enter the waste pits, the heated liquor then passing into the upper portion of the still, where the volatile ammonia is

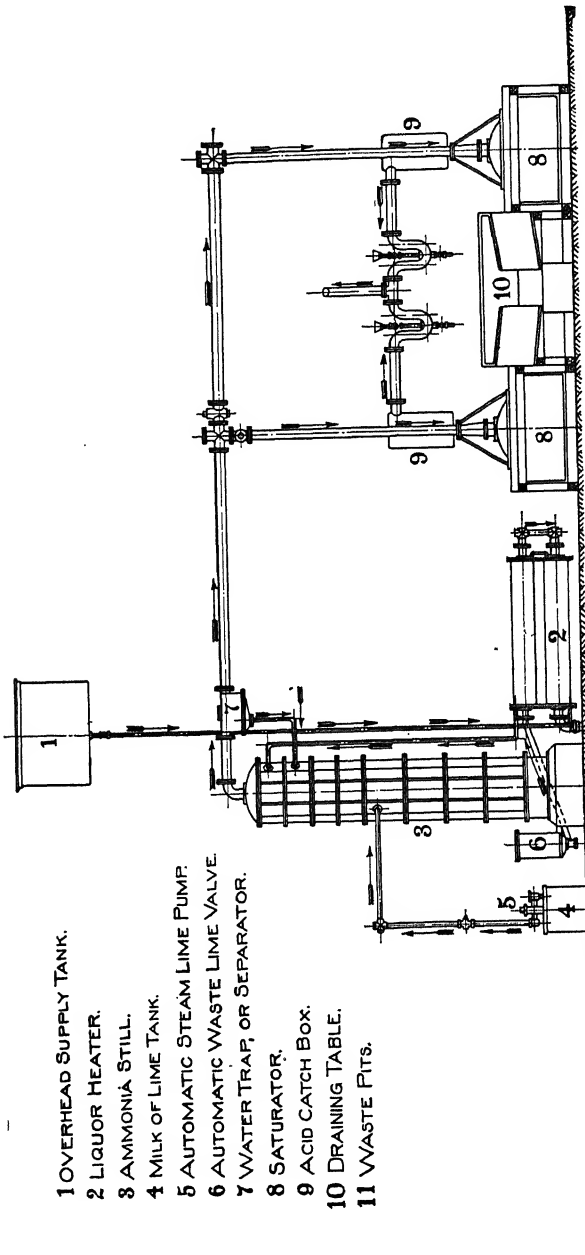


Fig. 21. — Indirect Sulphate Plant.

driven off, the fixed ammonia being treated with lime in the lower sections as described above. The water separator (7) serves to remove any condensed water from the ammonia gases, this condensate being returned to the still. The ammonia vapors now enter the saturator, this apparatus being lead-lined throughout, and are here brought in contact with sulphuric acid, whereby the ammonium salts are formed. These saturators are so constructed that they may be operated intermittently, the process being thereby interrupted while one saturator is being cleared of salt as the ammonia is diverted into the other, which has been prepared for the purpose in the meantime, or the process may be made continuous by entirely closing the saturator, feeding it regularly with acid, and removing the salts onto the draining table by means of a steam or air ejector.

The sulphuric acid employed is of 60° to 66° Bé., and in large works it is usually transferred by means of compressed air and a lead-lined monteju. Passing the sulphate from the drainage table through centrifugals dries it so that the salt contains practically no moisture, and it can be bagged for immediate shipment.

The indirect plant of C. and W. Walker, London, embraces a still column of square cross-section, the upper section being for free ammonia, the intermediate section being the liming chamber, while the lower sections take care of the fixed ammonia. The crude liquor flows from an overhead supply tank through the tubes of a vertical tubular heater, Fig. 21a, and there absorbs heat from the waste gases coming from the saturator. The tubes in the heater are provided with expansion joints at either end. The lime is mixed with water in a mixing tank provided with mechanical agitators, these agitators being driven from the pump which injects the lime milk into the still. The lower section of the still, as well as the liming chamber, is provided with perforated steam coils, steam being supplied to these coils through a reducing valve which maintains the desired pressure. Steam is admitted into the still through the lower coil, while the one in the liming chamber is used primarily to agitate the lime and thus cause it to mix properly with the liquor. The ammonia vapors coming from the still pass through a baffle box, where condensed water is thrown out, and then through an inverted U leg into the saturator. This saturator is

cylindrical in form, made of cast iron, with cone bottom lined throughout with lead, and is supported on four columns above the drain board. The ammonia inlet and the waste gas outlet are both located on the flat top of the saturator. The center of the top is provided with a clean-out opening of a diameter large enough to permit a man to enter the saturator to make repairs, and a lead curtain pipe depends from this opening and dips into the acid in the saturator, thus permitting access to the latter at any time. The saturator discharges through a special

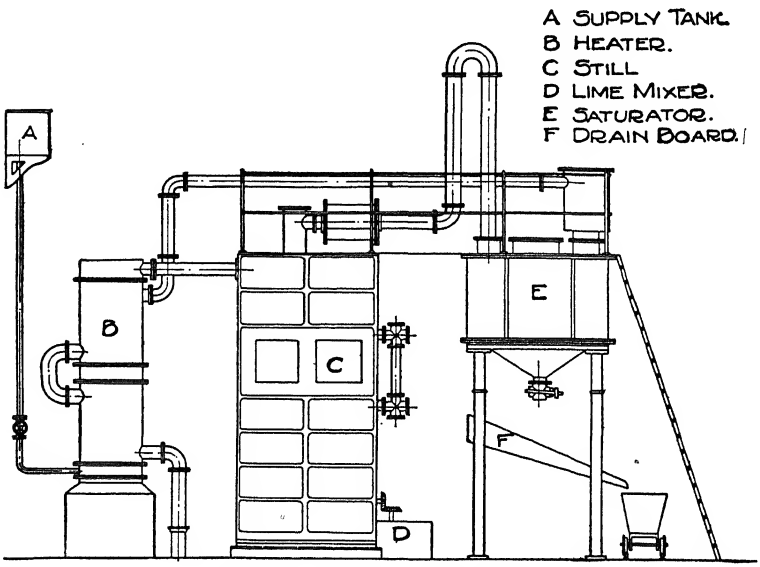


Fig. 21a.—Walker Sulphate Plant.

discharge valve made of copper, the valve consisting of a casing in which is mounted a plunger capable of a forward and backward motion through the medium of a lever. The discharge sulphate and the mother liquor are received on the drain board, the liquor being drained off to a cistern, while the sulphate is carried to a centrifugal dryer. It is claimed that the waste liquor from such a still contains less than 0.006 per cent of NH_3.

In the Wilton apparatus, also of English design, we find the raw liquor being run into preheaters, and from there to the stills, where they enter at a temperature of about 187° F., and at which point all volatile ammonia is liberated. The preheaters are tubular, made of cast iron, and heated by the ex-

haust gases from the saturators, these gases being almost entirely condensed by the time they leave the last heater. The construction of the still permits of easy access for cleaning, and the saturator, like that of Walker, is completely inclosed. It is of interest to note the method adopted for the removal of the salt, which is accomplished by means of a steam ejector. The bottom of the saturator is perfectly flat, except for a small sump in the center, in which the ejector is located. The NH_3 vapors enter the saturator through two pipes, passing vertically through the top, and entering the center of two crescent shaped perforated pipes which surround the well. The perforations are arranged in such manner that the vapor shoots downward towards the well, thus blowing all the salt into the well, and at the same time thoroughly mixing and saturating the acid bath. The mother liquor enters from a mother liquor pot and falls to the bottom of the saturator immediately behind the perforated pipes. The saturator is operated in the same manner as any other continuous saturator, the bath being maintained at about 32°–33° Bé. by a constant stream of acid flowing in, and the ejector may be kept in constant operation removing the salt, or the salt may be permitted to fill the well up to the spray pipes, when the ejector is set in operation intermittently. A bell and vent pipe are provided toward the discharge end of the ejector pipe to carry off the steam in order to prevent its escape into the house. After being ejected onto the drain-board the salt is dried in the usual manner.

EARNING CAPACITY OF AN INDIRECT SULPHATE PLANT

Capacity of the plant at 300 tons of coal per day, and 250 maximum working days, which at 5 pounds of ammonia per ton of coal will produce 727 tons of sulphate per year.

I. Labor:	
300 working days, 3 men at $2.00	$1800.00
20 days cleaning pits, 1 man at $1.50	30.00
Total labor	$1830.00
II. Materials:	
4500 M. pounds of steam at 20¢	$900.00
113 tons of lime at $8.50	960.50
727 tons of sulphuric acid at $11.50	8,360.50
Total material	$10,221.00
III. Miscellaneous:	
Drayage on 100 tons of sediment at 50 cents	$50.00
Illuminating the plant	60.00
Estimated repairs	500.00
Oil, waste, etc.	150.00
Total miscellaneous	$760.00

The total cost per year will then be:

I.	Labor	$ 1,830.00
II.	Material	10,221.00
III.	Miscellaneous	760.00
	Total	$12,811.00

making the cost of producing one ton of sulphate equal $17.62, and the net yearly income with a sulphate value of 727 tons at $60.00, equal to $43,620.00, will be $43,620.00 − $12,811.00 = $30,809.00, less depreciation and interest.

The unit charges given in the above three examples are of course dependent upon local conditions, and the quantity of materials used are the theoretical amounts; these conditions may change in each individual case, somewhat altering the net results.

The successful operation of a sulphate plant is dependent upon close attention to the character of the crude liquor, to the sulphuric acid, and to the lime used. While the chemical process is a very simple one, it is very sensitive to slight variations from the normal conditions, and derangements are therefore possible unless the required attention is given to the raw materials.

Clean liquor is a most important requisite, and this is especially true if closed saturators are used, the latter requiring that the crude liquor be entirely free of light oils and tar, or nearly so, this foreign admixture causing heavy frothing inside the saturator with a consequent deposition of a hard crust on the lead walls, which deposition leads to stoppages necessitating a shut-down and a complete cleaning of the plant.

In the purchase of sulphuric acid attention should be drawn to its content of iron and arsenic, as the acid should be as free of these foreign constituents as possible. The acid under no condition should be accepted if it contains more than 10 to 12 grains of iron per gallon, and the arsenic should not exceed 15 parts per million; besides this, the acid storage tanks should be subject to periodical cleaning. The lime used should also be as free from foreign matter as possible, and should analyze 95 per cent CaO.

The results of investigations made by K. Leo, and reported to the German Coke Commission, on a series of tests made

on the sulphuric acid used in producing the corresponding ammonium sulphates, is given in Table XIII, 60° Bé. acid having been used.

TABLE XIII. — INFLUENCE OF FOREIGN MATTER ON COLOR OF AMMONIUM SULPHATE

Content of foreign matter	Color of salt	Content of foreign matter	Color of salt
Tar oil + small quantity of tar, about 1.2 %	Dark gray-brown.	0.01 % Cd	White, with weak pale yellow tinge
Wash oil, but no tar, 1.2 %	White, with reddish tinge	0.03 % Cd	Light, reddish yellow
Wash oil + 0.01 % Cu	White	0.05 % Cd	Light, reddish yellow
		0.075 % Cd	Reddish yellow
0.01 % Cu	White	0.03 % Cd + 0.01 % Cu	Light gray
0.03 % Cu	White, with light grayish tinge	0.03 % Cd + 0.03 % Cu	Light gray
0.05 % Cu	White, with grayish tinge	0.03 % Cd + 0.03 % Pb	Light, reddish yellow
0.03 % Cu + 0.03 % As	White, with pale grayish tinge	0 03 % Pb	White
0.01 % As	White, with pale light yellow tinge	0.01 % Cu (CuS at point of oxidation)	White with pale gray tinge
		0.03 % Cu (CuS at point of oxidation)	Light gray
0.03 % As	Light yellow	0.03 % Cu (CuS partly oxidized)	White with grayish tinge
0.05 % As	Light yellow	0.03 % Cu from a strong acid bath	Light gray
0.03 % As + 0.01 % Cu	Red		
0.03 % As + 0.03 % Cu	Violet gray	0.04 % Pb from a strong acid bath	White
0.03 % As + 0.03 % Pb	Light yellow		

As stated before, ammonia is one of the principal by-products as well as source of revenue to the coal-gas producer, but as a rule the usual course of procedure is to manufacture concentrated liquor, only a few of the larger works having taken up the manufacture of ammonium sulphate. The competition of Chili saltpeter with sulphate

cannot last much longer, as these beds are gradually becoming depleted and the future will demand that this natural product be displaced by ammonium compounds.

As regards ammonia in liquid form, it may be prophesied that synthetic ammonia will in the near future be an active competitor, and if Germany, which produces about 40 per cent of the total ammonium sulphate made in England, Germany, and the United States, be taken as an example, we find that they work up about 22,000 tons of liquid ammonia per year, all of which can readily be replaced by synthetic ammonia at the present moment.

The drop in ammonia prices in Germany has been a cause of uneasiness for some time, and as synthetic ammonia continues to make inroads into the market this drop will probably become more marked, and difficulty will be experienced in finding a favorable market for this product; this condition will in all probability lead to a greater production of sulphate, the market for which is gradually increasing, as is witnessed by the fact that we are still importing quite an appreciable quantity of this product from Europe. Franz Buchner, Engineer of the Economic Association of German Gas Companies, advises his associates that synthetic ammonia production will necessarily lead to an increased sulphate production in gasworks practice, and recommends that smaller companies shall pool their ammonia liquor at some central point where sulphate can be prepared at less expense than if this were done by the individual. Table XIV shows the production and consumption of ammonium sulphate in the United States from 1902 to 1913: the amounts being expressed in tons of 2000 pounds, while Table XVI gives the world's sulphate production in tons.[1]

These figures show an increased production of 158,876 tons in the year 1913 over the year 1902, or an increase of 440 per cent; the increase in imports was largest in 1911, having been subject to a gradual increase, but this has declined since then; the consumption shows an increase of 208,366 tons in the year 1913 over that of 1902, an increase of 384 per cent. It is well to note here that in the figures

[1] American Coal Products Company.

TABLE XIV.— PRODUCTION AND CONSUMPTION OF SULPHATE IN THE UNITED STATES

Year	Production		Imported	Consumption
	By product coke ovens	Coal gas and carbonization		
1902	18,483	17,641 [1]	18,146	54,270
1903	24,098	17,775 [1]	16,777	58,650
1904	32,653	22,011 [1]	16,667	71,331
1905	41,864	23,432	15,288	80,584
1906	75,000 [1]		9,182	84,182
1907	62,700	36,609	32,669	131,978
1908	50,073	33,327	34,274	117,674
1909	75,000	31,500 [1]	40,192	146,692
1910	86,000	30,000 [1]	63,178	179,178
1911	95,000	32,000 [1]	103,743	230,743
1912	130,000	35,000 [1]	81,188	246,188
1913	153,000	42,000 [1]	67,636	262,636

[1] Estimated.

TABLE XV. — SULPHATE OF AMMONIA CONSUMPTION BY COUNTRIES

Year	United Kingdom. Gross tons	Germany. Metric tons	United States. Net tons	France. Metric tons
1900	65,000	127,700	36,011	49,000
1901	68,297	168,000	43,756	43,300
1902	63,750	175,000	54,270	53,300
1903	71,700	172,500	58,650	53,900
1904	68,500	200,000	71,331	53,800
1905	75,000	213,000	80,584	56,380
1906	82,000	229,500	84,182	67,000
1907	87,500	240,000	131,978	81,000
1908	90,000	260,000	117,674	84,000
1909	87,000	274,000	146,692	78,500
1910	87,000	350,000	179,178	73,086
1911	89,000	370,000	230,743	84,026
1912	90,000	425,000	246,188	..
1913	97,000	435,000	262,636	..

covering importations, the sulphate equivalent of the ammonia imported as chloride is included for the years 1912 and 1913.

TABLE XVI. — WORLD'S PRODUCTION OF SULPHATE IN TONS

Country	1905	1906	1907	1908	1909	1910	1911	1912	1913
England	273,550	294,170	318,400	330,450	354,747	373,590	391,160	394,540	426,745
Germany	190,000	235,000	287,000	313,000	330,000	373,000	418,000	492,000	548,558
United States	59,250	68,000	90,120	79,500	96,600	105,143	115,245	149,700	176,900
France	47,300	49,100	52,720	52,600	53,600	56,000	60,000	68,500	74,500
Belgium-Holland	24,200	30,000	[1] 55,000	35,000	40,000	43,000	43,000	50,000	51,000
Spain	10,000	10,000	[2] 12,000	..	12,000	9,000	..	..	..
Italy	4,500	5,000	11,000	80,000	12,000	12,000	166,500	175,000	161,500
Other countries	40,500	40,000	65,000	..	73,000	79,000	..	..	..

[1] Including Norway and Sweden. [2] Including Portugal.

Table XV shows the sulphate of ammonia consumption by countries, the amounts given including the equivalent of sulphate in other forms of ammonia.

The importance of these figures to the American sulphate producer can be seen when it is remembered that the total area of Great Britain, Germany, France, Austria-Hungary, Spain, Holland, and Belgium is about 992,180 square miles, with about 672,550 square miles under cultivation, and in the United States with its total of 3,026,800 square miles only 746,012 square miles are under cultivation, and the greater portion of the sulphate produced is used in fertilizer; a great deal of the land under cultivation in the States is still virgin soil, but this condition cannot continue, and nitrogen will have to be returned to the soil to make it productive.

In this connection it may also be well to state that in 1902 Japan imported 4000 tons of sulphate, while in 1907, or five years later, this amount was increased to 64,000 tons.

Diagram II, prepared by the Barrett Company, shows the price paid for ammonium sulphate from 1894 to the month of May, 1916; from this it is seen that the average price of sulphate during the twenty years prior to 1916 given in the diagram was $58.60 per ton, for the last ten years of that period $61.28 per ton, and for the last five years $61 per ton.

During the last fifteen years the attention of investigators has been turned towards an endeavor to simplify the methods used to produce ammonium sulphate from the product due to coal distillation, and instead of treating the gas liquor itself, as in the old or indirect system just described, the endeavor has been to pass the gas directly into and through the saturator, which is a closed one in this case; this method of procedure has been termed the "direct process" and, as the name indicates, it is a reversal of the old method. Other investigators have proceeded along somewhat different lines, and while passing the gas through the closed saturator, they at the same time vaporize the ammonia produced by previous condensation and then pass these vapors into the saturator in conjunction with the gas, this latter development being known as the "semi-direct" process.

Other investigators, such as Burkheiser and Feld, make use of the sulphur contained in the gas, thus doing away with the saturator and its bath of acid, this being the only real "direct" process, as it is entirely independent of the use of sulphuric acid. While the Burkheiser process has been tried in an experimental way at Tegel, Germany, it has so far, to my knowledge, not been successful, and the experiments at that plant have been abandoned. The principal direct processes in active operation are those of Brunck, Otto, and Feld, while those of the semi-direct procedure are known as Koppers, Mont Cenis, Collin, and Still.

The first process on the "direct" principle was devised by Franz Brunck, of Dortmund, Germany, and his successful experiments began about fifteen years ago, making Brunck the father of all of the "direct" or "semi-direct" systems with the exception of the Feld. Brunck's first plant was erected at the Kaiserstuhl works in Dortmund, being designed to treat 2,750,000 cubic feet of coke-oven gas per 24 hours, the gas containing from 150 to 195 grains of ammonia per 100 cubic feet at a temperature of from 80° to 95° F. Brunck passed this cooled gas through an acid washer, the washer being filled with earthenware cubes measuring about three inches to the side; these cubes were constantly sprayed with sulphuric acid, the resultant liquor flowing from the bottom of the washer being returned to the sprays

until it possessed a certain degree of concentration, after which the acid liquor was removed to the saturator where the salt was formed. This plant was also provided with a still for vaporizing the ammonia thrown down by previous condensation, these ammonia vapors meeting the acid liquor in the saturator.

This plant led to a further development by Brunck, and his revised method of operation is as follows: — The hot, raw gas is first passed through a temperature regulator, one or more being used according to circumstances, and then into a tar centrifugal; after the gas has thus been brought to a temperature of from 255° to 265° F., and after about 80 per cent of its tar has been removed, it is passed into the saturators of the ammonia plant. Here the ammonia reacts with the sulphuric acid and a further 10 to 15 per cent of the tar is extracted, after which the gas passes through washer-scrubbers and then through volumetric condensers, where the gas is sprayed for the removal of naphthalene, and then on through tubular condensers and exhausters. While this process seemed successful at the time, another development was soon due, brought about by the introduction of the closed saturator, as the open saturator permitted both the gas and the liquor to cool too rapidly, this fact having compelled Brunck to maintain the temperature of the gas ahead of the saturator at about 255° F.

The application of the closed saturator permitted a lower gas temperature, thereby bringing about a more efficient extraction of tar, a temperature of only 185° F. ahead of the saturator also simplifying the apparatus.

As stated above, Brunck's success soon led to developments by other investigators producing some direct and some semi-direct processes, and one of the most successful of the latter type is the

Koppers System:

The Koppers process (Fig. 22) is termed a semi-direct one because the gases are freed of tar and some ammonia by cooling before they enter the acid bath, the condensed ammonia being afterwards vaporized. Koppers grounded his theory on the hypothesis that the gas could not be freed of tar by mechanical means only, and that cooling was

necessary in order to accomplish this, and having a tar-free gas he was thus able to bring the dew point of the gas to a rather low temperature.

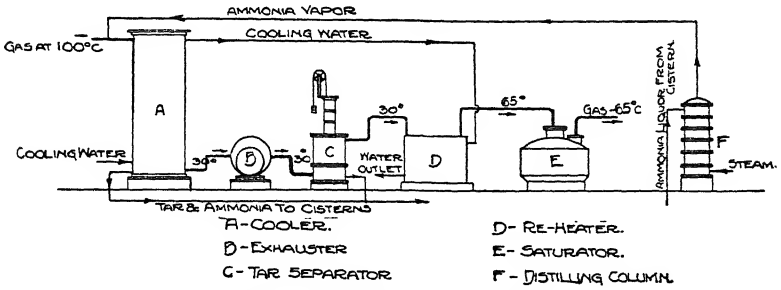


Fig. 22. — Koppers Sulphate Plant.

In this process the gases coming from the hydraulic main enter a cooler, where a portion of the tar, as well as condensed water, is removed; about one-half of the cooling system is used to effect the temperature transfer between the raw gas and the cooled, tar-free gas. After the gas has passed through the last tubular water condenser it passes into the temperature transfer apparatus, where it is preheated and then removed by means of an exhauster and sent into a Pelouze, where the last portion of the tar is removed and the gas made practically tar free.

Koppers also includes a temperature regulator in his system, locating it between the Pelouze and the saturator, this apparatus also being a preheater, and its use is of great benefit to the entire process. The gas is now admitted into the saturator where it reacts with the acid in the usual manner. The condensate from the coolers (tar and ammonia) is run into a separator where, due to their respective specific weights, the tar and liquor separate, the liquor being conducted to a still where it is vaporized by means of steam and lime in the usual manner. The ammonia vapors coming from the still are not conducted directly into the saturator, but to the gas main ahead of the coolers, as Koppers considers this method of more value, and its adoption in practice seems to have borne out this opinion.

The advantages of this process over the old or indirect one

are self-evident; they consist in simplicity of operation and ease of supervision, the saving of steam in the ammonia plant, owing to the fact that it is not necessary to distil off all of the ammonia contained in the gas, and the obviation of all mechanical washers for removing ammonia from the gas.

The saving of steam, however, only holds good for evaporative purposes, as steam or power of some kind is required at the exhausters in addition to what would be required with the indirect system; and this holds good for all of those systems which admit the gas directly into closed saturators, as they throw a back pressure of many more inches, due to the depth of the bath, than would ordinarily be the case, and to which reference will be made later.[1]

The Collin Process:

The semi-direct process introduced by Collin of Dortmund, Germany, is shown in Fig. 23; this system is very similar to that of Koppers, the specific difference between the two being that Collin does not use a temperature transfer apparatus nor a gas preheater between the tar extractor and exhauster.

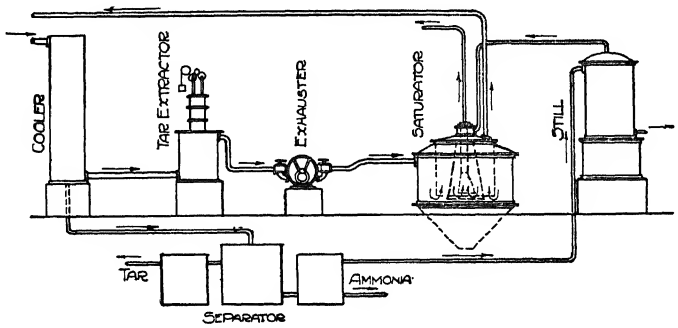


Fig. 23. — Sulphate Plant — "Collin" System.

The gas coming from the hydraulic main is reduced in temperature in the cooler to a degree which will permit of efficient tar extraction in the Pelouze; the exhauster then transfers the tar-free gas to the saturator, where the am-

[1] See "The Cleaning of Blast-Furnace Gases," McGraw-Hill Book Co., Inc.

monia is absorbed by the acid bath. The condensate thrown down in the cooler is distilled in the usual manner in vaporizing stills, and the ammonia vapor thus produced is sent into the saturator in such manner that it cannot unite with the gas coming from the hydraulic main. Due to the pressure produced in the still, the waste gases formed there pass through the acid bath by means of their own pressure and are caught under the central bell of the saturator, from whence they pass on to the stack, or join the fuel gases going to the coke ovens in a coke plant. Collin claims that this procedure prevents adding sulphur vapors to the gas. Due to the separate admission of the vapors from the still to the saturator bath it is possible to carry out the process of sulphatation without heating the bath by external means.

Collin states that it is of distinct advantage not to carry the troublesome waste gases away with the other gases, as Koppers does, but to carry them directly to a stack, which latter procedure is made possible by the construction of the Collin saturator.

In another system devised by Collin, Fig. 23A, the gas from the hydraulic main is caused to pass through tubular water coolers where the greater portion of the tar and ammonia is precipitated, after which it passes through a P. and A. Condenser for the removal of the remainder of the tar. After being thus freed of tar and ammonia, corresponding to a temperature of 113° F., the gas being of 212° F. as it enters the first coolers, the gas passes into a second set of water coolers of similar construction to the first set, where it is cooled to about 73° F., and from thence through the exhausters to the saturators.

In this system Collin uses two saturators, set at different levels in the building, the cleaned gas entering the upper saturator at about 73° F. and leaving it at 100° F.; the bath in this saturator is of about 25 per cent free acid, the liquor from this bath being used as a saturating medium in the lower saturator, the latter receiving the ammonia vapors from the still.

Collin claims that this arrangement of saturators, or the separation of the direct gas from the still vapors, eliminates the obnoxious vapors of H_2S, $(CN)_2$, etc., from the system.

The Still Process:

In this system the gas passes the cooling water in a counter current, coming in direct contact with it, thus being cooled itself while simultaneously heating the cooling water, the quantity of the latter being increased by the amount of water condensed from the gas, this water being used later to raise the temperature of the gas in the same direct manner, and Still claims that the water condensed from the gas is thus vaporized back into it.

This system is shown in Fig. 24; the gas from the hydraulic main enters the condenser (*A*) at (*a*) with a temperature of 176° F., where it comes in direct contact with a counter stream of water and is thus cooled. This condenser is of very large dimensions, in some

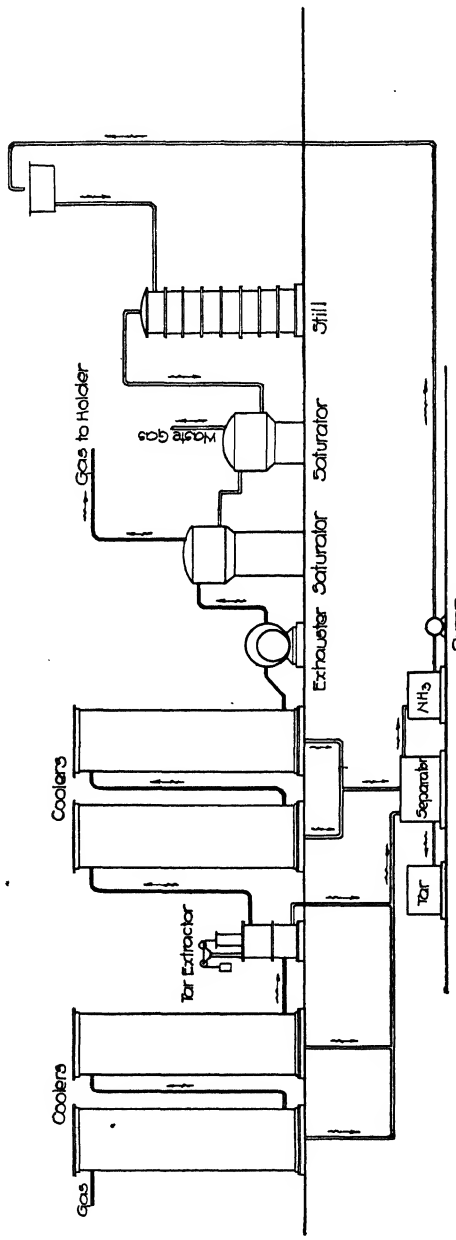


Fig. 23A.—Collin Sulphate Plant.

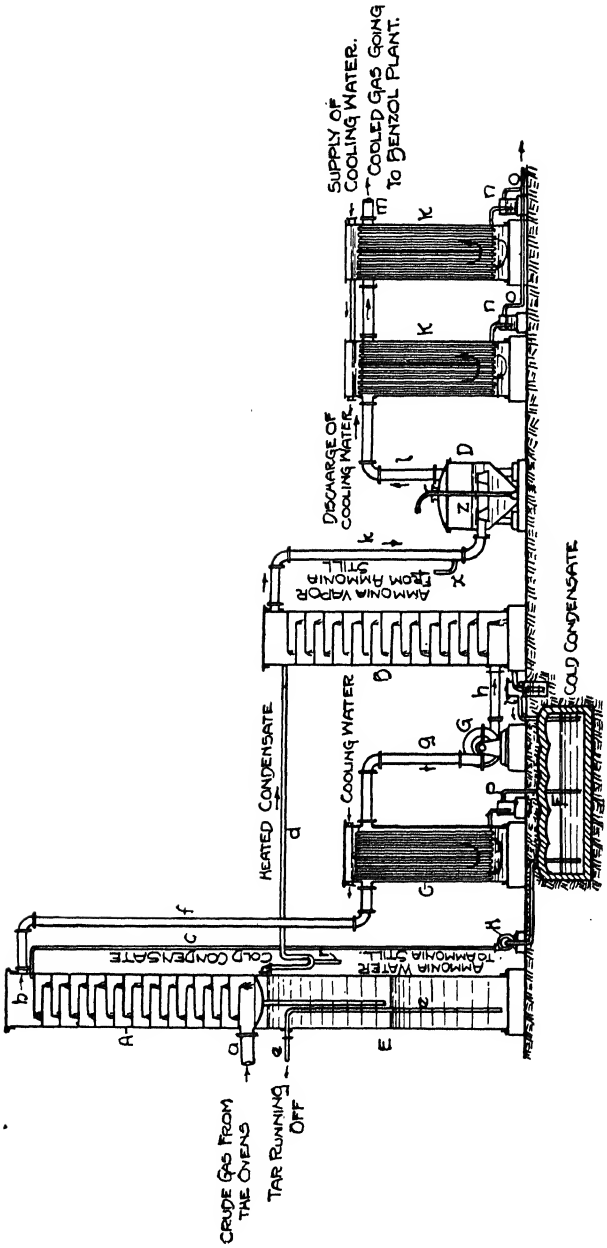


Fig. 24. — Still Sulphate Plant.

cases being 10 feet in diameter and 82 feet high, the lower portion (*E*) acting as a receiver and separator for the products of condensation. The upper or cooling portion of the tower is provided with a number of perforated plates (*b*), the condensing water trickling through the holes and over the edge of the plates, this water being circulated by means of the pump (*H*) and pipe (*c*). The gas is thus cooled to 85° to 95° F., while the water is heated to approximately the same temperature as that of the entering gas. Still claims that this method of cooling removes the entire content of tar and naphthalene, as well as the greater portion of the water vapor from the gas.

The warm water, tar, etc., collect in the receiver (*E*), where they are separated due to their respective specific gravities. The tar is run off by pipe (*e*) directly to the tar storage, while the warm water passes through the syphon (*d*) to the reheater (*B*). The cooled gases now pass through pipe (*f*) to a second cooler (*C*), of the tubular type, where they are further reduced in temperature to from 68° to 77° F. This second cooler is for the purpose of maintaining the final temperature of the gas at a constant point, and Still claims that this second cooler is the regulator governing the proper performance of the plant.

The gas leaves the second cooler through pipe (*g*) and is forced by the exhauster (*G*) into the reheater (*B*); here the gas is brought into direct contact with a most minute spray of warm water, thus heating the gas to about 158° F., while the water is cooled down to about 85° to 95° F., or approximately to the temperature of the entering gas. The water passes off into the storage tank (*F*), from whence it is again pumped into the cooling tower (*A*), thus continuously extracting heat from the gas and in turn giving this heat back again, a portion of the ammonia in the gas being thus absorbed also (Still claims 120 to 180 grains per gallon of water), and as soon as this degree of concentration is reached no more ammonia is absorbed, and the entire content of ammonia remaining in the gas is carried through the remainder of the process. A certain portion of the absorbed ammonia is removed from time to time and evaporated by means of steam and lime in the usual manner, the ammonia

vapors thus produced being mixed with the gas leaving the reheater and passing on through pipe (*K*) into the saturator (*D*), where the ammonia is absorbed by the sulphuric acid.

The temperature of the gas entering the saturator is sufficiently high to prevent the precipitation of water vapor, and thus permits of direct sulphatation without the addition of external heat. The salt is ejected from the saturator onto a draining table and then dried in the usual manner. The gas leaves the saturator at a temperature of about 176° F. and then passes into the final coolers (*K*).

The Coppée Process:

In this process, shown diagrammatically in Fig. 25, the

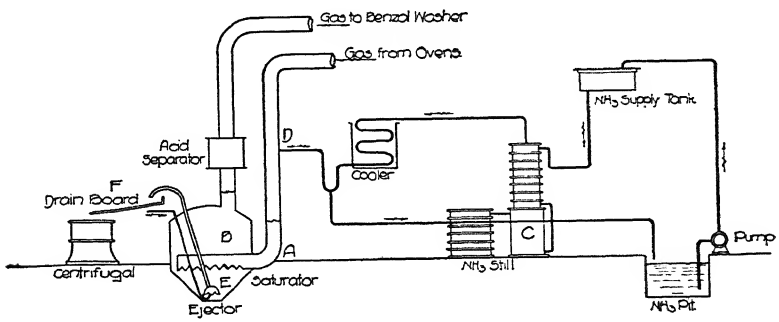


Fig. 25. — Coppée Sulphate Plant.

gas coming from the hydraulic main is cooled down in the usual condensers to about 90° F., after which it is passed through a Pelouze condenser for the extraction of the remainder of the tar. The tar-free gas is then passed directly into the inclosed lead saturator (*B*) at (*A*), where the ammonia combines with the acid. The ammonia liquor condensed by the process of cooling is distilled in the still (*C*), the ammonia vapors from the still being passed into the gas main at (*D*) directly in front of the saturator, while the heat of the reaction in the saturator prevents any further condensation at that point. This process, like the others of its class, is continuous and only requires attention when fresh acid is needed and when sulphate is to be removed and dried. The sulphate is ejected from the saturator in the usual manner by either a steam or an air ejector at (*E*),

thus delivering the salt to the draining table (*F*), from whence it passes into the centrifugal and thence to storage. This process claims that a reheating of the gas is not necessary after it has once been cooled to 90° F.

The Mallet Process:

The Mallet system is one of the latest and it differs from all other acid bath systems in several particulars, but closely

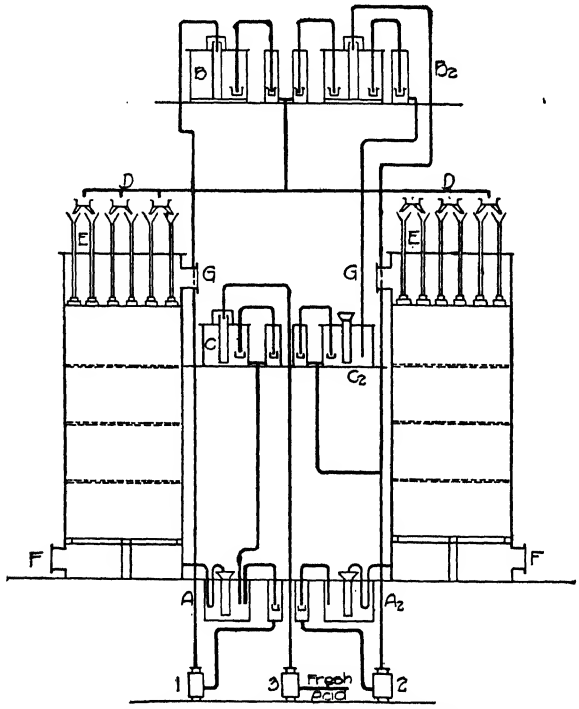


Fig. 26. — Mallet Sulphate Process.

resembles Brunck's early acid washer process. In its operation, the gas is cooled and then passed through a tar extractor in the usual manner, after which the tar-free gas is conducted into an acid washer (see Fig. 26), this washer being built somewhat like a Glover tower, in that it consists of a lead shell the inside of which is supplied with earthenware pipes or tubes, down which the cool acid is caused to trickle, this acid being of 53° Bé. strength.

The tower is built up of lead rings burned to each other, the bottom resting on a cast-iron base, also lined with lead, encased in the masonry foundation, the entire tower being supported by means of timber framing. The tubes (Fig. 27), are small pipes 4 inches high, 3 inches external and 2 inches internal diameter, forming concentric rings supported upon lead-covered iron bars, thus forming a floor located about 20 inches above the bottom of the washer, the washer usually being about 9′9″ in diameter and 19′6″ high.

At the top of these stacks of tubes are placed three rows of earthenware cupels (Figs. 28 and 29), which in turn support

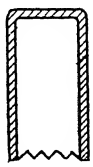


Fig. 27.

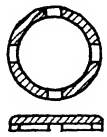


Fig. 28.

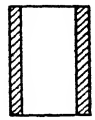


Fig. 29.

pots for the purpose of splitting up the gas; these pots are also of earthenware and are supplied with serrated edges, receiving the washing acid from the lead tubes (*E*) (Fig. 26), these latter tubes having an internal diameter of about three-quarters of an inch, being burned to the lead cover of the tower.

The flow of the acid is regulated in such manner that each tube (*E*) receives the same amount of acid, thus causing the entire washing surface to be sprayed uniformly. The acid is distributed through the medium of the channels marked (*D*), from whence it is sprayed by means of plungers in the (*E*) tubes over the whole internal surface of the washers. This distribution of the acid causes it to flow over the pipes, thus coming into intimate contact with the gas, the latter entering the washer at (*F*) and leaving at (*G*).

The acid mother liquor leaves the bottom of the washers and is collected in the lower tanks (*A*) and (A_2), from whence it is pumped by pumps (1) and (2) into the elevated tanks (*B*) and (B_2). When this acid mother liquor has received a sufficient degree of ammonia concentration, a certain portion is withdrawn and conducted to the intermediate

bath (C_2), from which it drains to the saturator, where it combines with the ammonia remaining in the gas and with the acid.

The usual troubles with impure sulphuric acid in the saturator are said to be avoided in this system, because the acid is subjected to a complete purification by means of the hydrogen sulphide in the gas, during its passage through the tower washer, precipitating arsenic sulphide, which floats on top of the acid in the bath (A) and (A_2) and from whence it may be removed by means of a ladle.

The absorption of ammonia is said to be practically complete up to 0.25 grain per 100 cubic feet of gas, and it is claimed that the back pressure thrown by the tower washer is only 1 to $1\frac{1}{2}$ inches of water.

The Mont-Cenis Process:

In the Mont-Cenis system, shown in Fig. 30, the gas is cooled in the usual manner in a cooler (A), the temperature

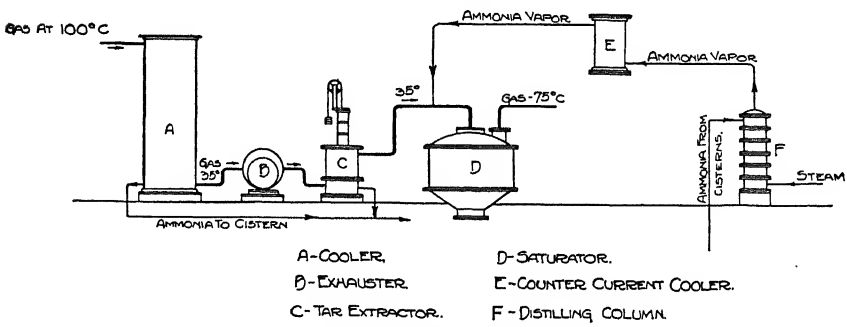


Fig. 30. — Mont-Cenis Sulphate Plant.

of the gas entering the exhauster (B) being reduced to about 95° F. The condensate from (A) is run off to a separating well, where the tar and ammonia are separated by specific gravity. From the exhauster the gas enters the Pelouze (C), where the remainder of the tar is removed, and then enters the saturator with a temperature of 95° F.

The ammonia from the well is pumped into a still, where it is treated with steam and lime, the vapors passing through a counter-current cooler (E) where the water is thrown down, after which these vapors enter the saturator in conjunction

with the gas, the chemical reaction in the saturator increasing the temperature of the off-going gas to about 169° F.

A peculiarity of this system is that a layer of well-distilled tar, about one to two inches thick, is poured on top of the acid bath in the saturator, this tar being for the purpose of preventing a too violent agitation of the acid bath during the formation of salt; it is claimed that this addition of tar does not affect the quality or cleanliness of the salt, providing the gas itself is free of tar.

The Otto Process:

In the Otto process all ammonia washing and ammonia liquor distillation is obviated, and the advantages of this process lie in the saving of steam and water, and in the simplicity of supervision.

The greatest difficulty which had to be overcome in the development of this process lay in separating the tar fog from the hot gases, and many experiments in direct sulphatation failed on this account. The adoption by Otto of the tar washing spray, operating at temperatures which closely approach the dew point of the gas, finally brought about the desired results.

All substances which can be separated from the gas are removed after the gas has passed the tar sprays, and only such hydro-carbons as are due to the prevaling temperatures are carried forward with the gas to the saturators and coolers. Due to intensive cooling and consequent decrease in volume, water vapors, light fatty oils, and naphthalene are condensed and, due to their difference in specific gravity, these substances can be readily separated from each other.

The tar oils separated at this point are of great value as wash oils for benzol recovery, and therefore have a value of three to four times that of the remaining tar. The acid in the saturator has no effect upon these condensates, and also does not affect the benzol-carbon formation in the gas. With a normal coal and proper cooling the tar oils dissolve the naphthalene thrown down, and it is claimed that stoppages are thus avoided.

This system is shown in Fig. 31, and the method of operation is as follows: — The gases coming from the hydraulic

main, and which have been subjected to atmospheric cooling during their passage, have a temperature of from 212° to 248° F., and they thus pass through an envelope surrounding the saturator (Fig. 32), after which they pass into the tar-spraying device, the latter being constantly supplied with tar by means of a rotary pump. Due to the intimate contact between tar, or tar liquor, and the gas, a practically tar-free gas is produced.

From the tar-receiving tank a portion of the separated tar flows through an overflow to the tar-storage pit, and another portion passes on to the rotary pump, which latter again pumps the hot tar into the spraying device. The pipe connections on the discharge side of this pump are so arranged as to permit the temperature of the washing tar to be kept at any desired degree, thus maintaining the temperature at which the tar is separated at the dew point. Under normal conditions this dew point is at about 169° F., while the temperature of the tar, due to atmospheric changes, varies between 122° and 176° F.

The tar-spraying apparatus is provided with a number of sprays so arranged that they can be cut out at will, thus making the tar extractor readily adaptable to fluctuations in manufacture.

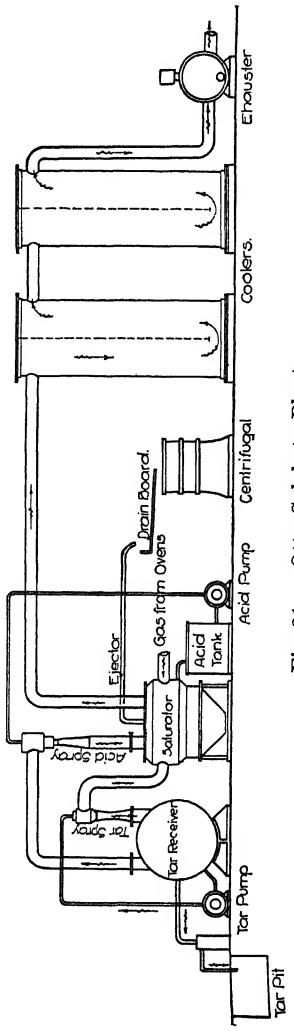


Fig. 31. — Otto Sulphate Plant.

After the tar has been removed the hot gas, with its entire content of water vapor and ammonia, is led into the closed saturator through a submerged bell, being sprayed with sulphuric acid in the downpipe leading to the saturator

(see Fig. 32). The lower edge of this bell is serrated, and the saturator is only partially filled with sulphuric acid. In the saturator, due to the heat of reaction as well as to the heat transmitted by the raw gas in passing through the envelope, the temperature of the incoming gas is increased, this increase being sufficient to prevent dilution of the bath by condensation.

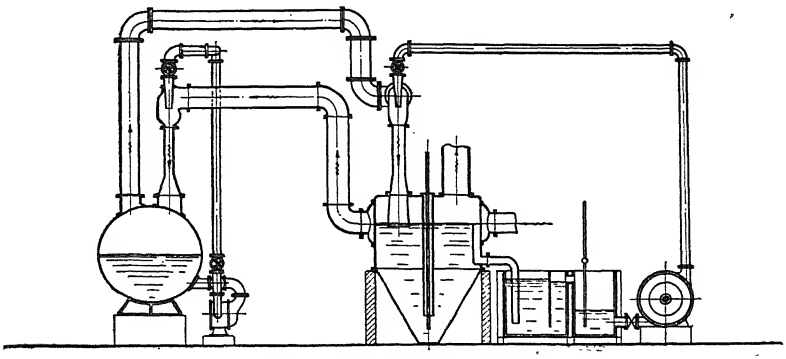


Fig. 32. — Otto Sulphate Plant.

After proper saturation the salts fall to the bottom of the saturator, being removed from there onto the draining table by means of an ejector, going from thence to the centrifugal and finally to storage.

The Strommenger Process:

Strommenger claims that many of the direct acid bath systems have failed to measure up to expectations due to inability to entirely expel the tar from the gas, and that in order to produce a saleable sulphate it is absolutely necessary to remove all traces of tar before the gas is admitted into the acid bath; he also claims that the usual devices are only partially successful in the removal of tar, which fact has led him to devise a new form of extractor, stating that the use of this device entirely eliminates the tar and produces a perfectly clean salt. This extractor also makes use of hot tar as a washing medium, the hot tar entering the lower half of the extractor, where it is broken up into a number of fine tar streams in such manner as to bring the gas into intimate contact with the hot tar; the gas then ascends into

the upper half of the extractor, where this process of contact between gas and hot tar is repeated, the tar circulating in a direction counter to that of the gas, the latter also being broken up into fine streams in order to increase contact.

The upper portion of the extractor is provided with a filter, the gas being compelled to pass through it, thus preventing the carrying forward of any entrained tar.

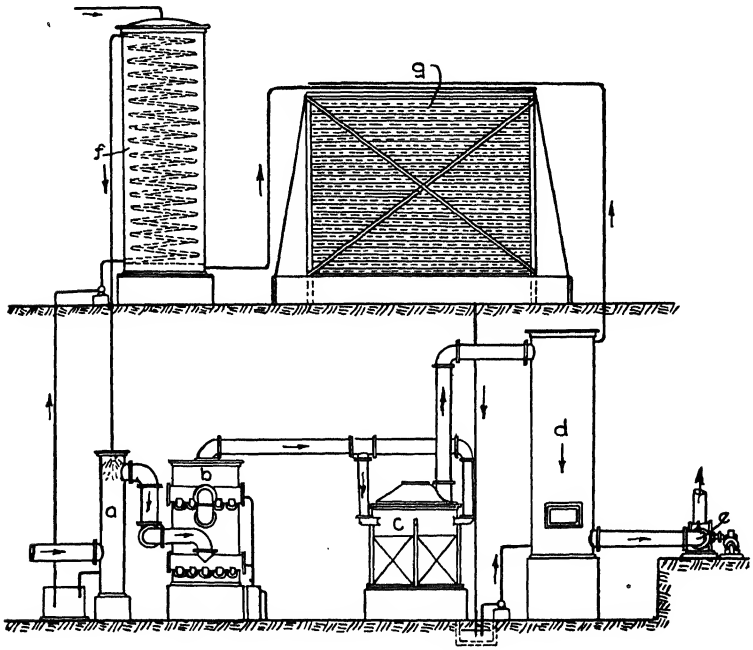


Fig. 33. — Strommenger Sulphate Plant.

It is claimed that at the Phœnix Colliery, Germany, the tar was completely removed from the gas by means of this extractor, but that with a temperature a little higher than that for which the extractor was designed, the gas retained about eleven grains of tar per 100 cubic feet, a degree of cleanliness which can be equaled by almost any well-designed machine.

In the sulphate process proper (Fig. 33), the gas from the hydraulic main enters the temperature regulator (*A*), where its temperature is brought to the desired degree, after which

it enters the tar extractor (*B*). The wash tar required in the extractor is constantly replaced by the tar expelled from the gas, and all surplus tar is conducted to storage. The ammonia liquor used in the temperature regulator is transferred to the cooler (*F*), where it is cooled and such part as is sent to the saturator is replaced by fresh liquor. The water required in the cooler is later cooled on the open frame (*G*), or it may be used for other purposes.

The gas, freed of tar, now enters the saturator (*C*), where ammonia is extracted by combination with the acid, the gas being then transferred by the exhauster (*E*) through the final cooler (*D*) for further treatment.

The Feld Process:

In all of the systems thus described we find the necessity of using sulphuric acid, and as the production of one ton of ammonium sulphate requires approximately one ton of sulphuric acid, the cost of this acid becomes an important feature of manufacture, and it is therefore of general interest to be able to produce sulphate in a manner which makes the producer independent of the sulphuric acid manufacturer, or, instead of using acid, to make use of the hydrogen sulphide contained in the gas and to combine it with the ammonia in the formation of ammonium sulphate.

For many years various investigators attempted to combine ammonia direct with sulphurous acid, and as far back as 1852 a British patent was issued to Laming on this subject. Claus, in England, about 50 years ago tried to remove the hydrogen sulphide from the gas by washing the latter with ammonia, and then to regenerate the resultant solution of sulphur, ammonia, and ammonium carbonate by heating, using the remaining ammonia solution for wash purposes; the high carbonic acid content of the gas required, however, that a volume of ammonia equivalent to about six times that originally contained in the gas should be in constant circulation, thus producing an ammonia loss which prevented the successful introduction of this system.

Laming, Claus, and the others who were working along similar lines overlooked the fact that the reaction by which ammonia and sulphur dioxide combine will not proceed until

the reaction is complete. Neutral ammonium sulphite, $(NH_4)_2SO_3.H_2O$, gives off ammonia, and the quantity of ammonia given off increases with the temperature, the residue being a wet acid salt, or $(NH_4)_2HSO_3$, which, in contact with air, will give off sulphur dioxide, and only a small portion will be changed into sulphate.

This behavior of the sulphites is due to the high vapor tension of both ammonia and sulphur dioxide, and for this reason it becomes impossible to completely absorb the ammonia contained in the gases by means of an aqueous sulphurous acid solution, or to completely absorb sulphur dioxide contained in gases by means of an ammonia solution.

Even if these difficulties could be overcome in practice, the resulting salt would be of very unstable nature. To use ammonium sulphite directly as a fertilizer, as proposed in Lachomette's British patent of 1887, is impracticable for more than one reason, the principal one being its tendency to give off sulphur dioxide and ammonia to the atmosphere, and attempts to change ammonium sulphite into ammonium sulphate by contact with air have proven to be abortive.

For many years Feld experimented with the reactions occurring between sulphur dioxide and hydrogen sulphide; he found these reactions rather complicated, although the equation usually and erroneously assumed for it,

$$2H_2S + SO_2 = 2H_2O + 3S,$$

is simple enough.

In the course of these researches Feld established the fact that certain tar oils are excellent solvents for sulphur dioxide and sulphur; pure sulphur dioxide introduced into heavy tar oils is eagerly absorbed, and causes a strong evolution of heat. If this absorption is carried out in a closed, agitated bottle, the reaction will be so energetic that the atmospheric pressure above the liquid is considerably reduced, while the temperature rises.

Now, if a tar oil has been saturated with sulphur dioxide, and pure hydrogen sulphide is then passed into it, the latter will also be completely absorbed, while the temperature

increases and the pressure decreases. In this case the sulphur dioxide and the hydrogen sulphide react, forming sulphur and water, and the sulphur dissolves in the hot tar oil.

If the tar oil is now treated alternately with sulphur dioxide and hydrogen sulphide, a portion of the dissolved sulphur will in time crystallize out of the saturated oil as a crystalline grain.

While this process appears to be very simple, it involves great difficulties when applied to gases containing sulphur dioxide and hydrogen sulphide in very dilute form.

Further experiments showed that hydrogen sulphide decomposes zinc thiosulphate in such manner that zinc sulphide and elementary sulphur are formed, or

$$ZnS_2O_3 + 3H_2S = ZnS + 3H_2O + 4S.$$

If concentrated or dilute hydrogen sulphide is introduced into a solution of ZnS_2O_3, the hydrogen sulphide will be completely absorbed, and in experiments carried out on a working scale with illuminating gas, which had been practically freed of ammonia, one washer was sufficient to absorb from 80 to 90 per cent of the hydrogen sulphide in the gas by means of a zinc thiosulphate solution.

Feld's idea was to regenerate the zinc thiosulphate from the zinc sulphide by means of sulphur dioxide according to the equation,

$$2ZnS + 3SO_2 = 2ZnS_2O_3 + S,$$

but after repeated attempts this had to be abandoned because the process of regeneration could not be made complete. The zinc sulphide dissolves very slowly in the presence of sulphur dioxide, and the regenerated zinc solution loses most of its ability to absorb hydrogen sulphide; the regeneration process does not take place in the manner expected because when zinc sulphide and sulphur dioxide react, polythionate, or ZnS_4O_6 is mainly formed instead of the expected thiosulphate ZnS_2O_3, and hydrogen sulphide acts strongly on zinc thiosulphate, but only slightly on zinc polythionate.

In spite of these shortcomings this process indicated a direction which ultimately led to success, and it also indi-

cated the possibility of simultaneously absorbing hydrogen sulphide and ammonia from the gas in accordance with the equation:

$$ZnS_2O_3 + 2NH_3 + H_2S = ZnS + (NH_4)_2S_2O_3,$$

and further experiments confirmed this surmise.

The difficulties met with in attempting to regenerate the ZnS to ZnS_2O_3 were, however, too severe, and recourse was then had to an iron salt, FeS_2O_3, which was used in place of the zinc salt for absorption purposes.

In this latter case the gases containing ammonia and hydrogen sulphide were washed with a solution of FeS_2O_3, or iron thiosulphate, whereby iron sulphides were precipitated according to

$$FeS_2O_3 + 2NH_3 + H_2S = FeS + (NH_4)_2S_2O_3.$$

This iron sulphide, FeS, was then dissolved in sulphurous acid, thus again forming FeS_2O_3 which was then returned to circulation for a further treatment of the gas, or

$$2FeS + 3SO_2 = 2FeS_2O_3 + S.$$

When this alternate treatment of the solution with gas and then with sulphur dioxide had been repeated a number of times, the content of ammonium salt increased to such an extent that the recovery of ammonium sulphate from the solution became profitable.

The treatment of thiosulphate with sulphurous acid produces polythionate, or

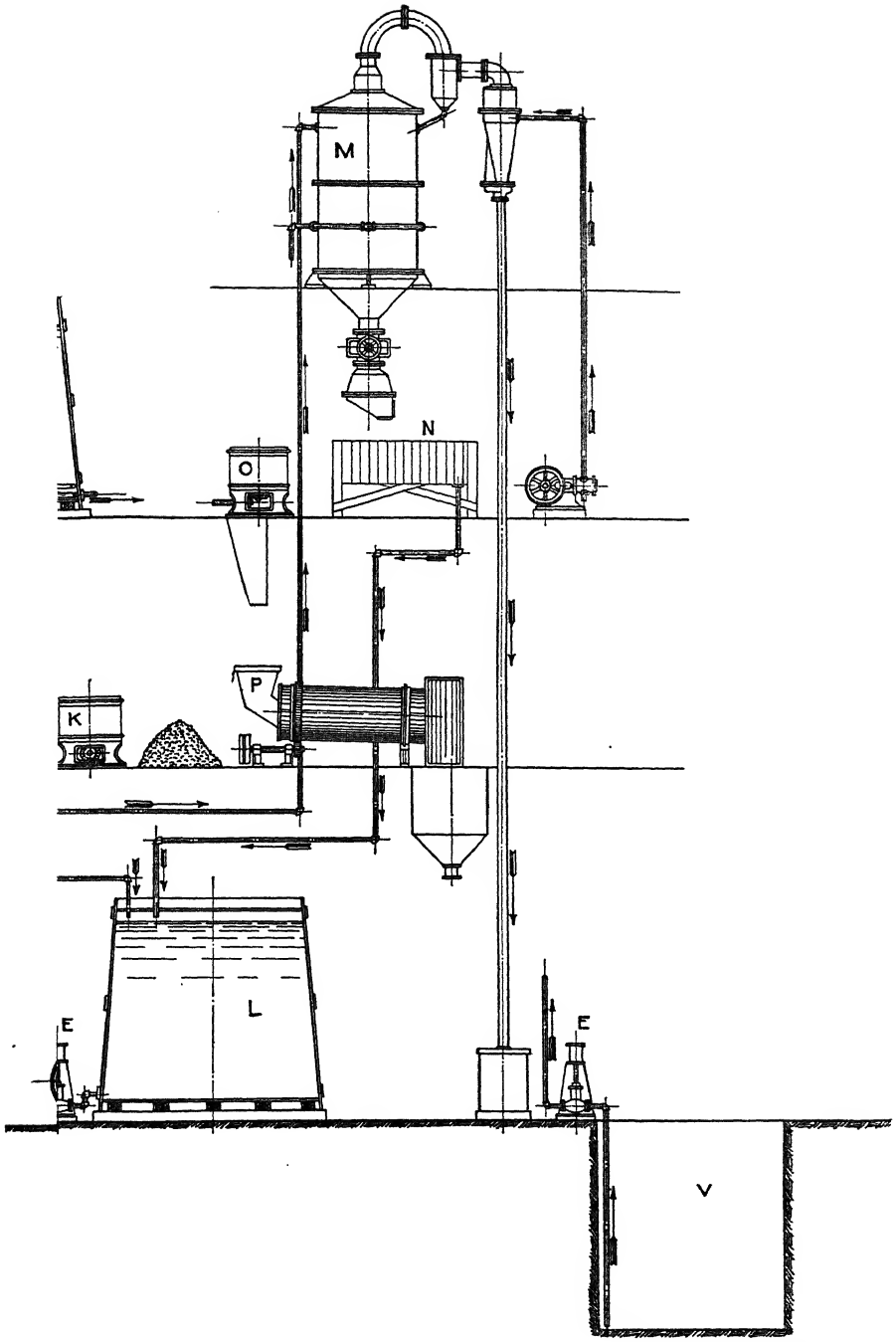
$$FeS_2O_3 + (NH_4)_2S_2O_3 + 3SO_2 = FeS_3O_6 + (NH_4)_2S_4O_6,$$

and this solution being heated gave ammonium sulphate, or

$$FeS_3O_6 + (NH_4)_2S_4O_6 + \triangle = FeSO_4 + (NH_4)_2SO_4 + 2SO_2 + 3S.$$

The heating of the solution may be done simultaneously with the treatment with sulphurous acid, so that the last reaction takes place simultaneously with the preceding one.

The formation of ferrous sulphate in this process is accompanied by the formation of sulphur dioxide and free sulphur, the latter being burned in a sulphur burner to again form



(*Facing Page 132*)

sulphur dioxide for regenerative purposes while the sulphate solution is again treated with crude gas, or

$$FeSO_4 + 2(NH_4)_2SO_4 + 2NH_3 + H_2S = FeS + 3(NH_4)_2SO_4,$$

the solution thus increasing in sulphate content with each treatment, and when the solution had reached a certain degree of ammonia concentration the liquor was evaporated with the consequent formation of salts.

The successful operation of this process both in Germany and in the United States led to further investigations, particular attention being paid to sodium and ammonium salts. Feld thus found that ammonium thiosuphlate has the characteristic property of being very easily changed into polythionate by treating it with sulphur dioxide, or

$$2(NH_4)_2S_2O_3 + 3SO_2 = (NH_4)_2S_4O_6 + (NH_4)_2S_3O_6,$$

and this led to the adoption of the present process as shown diagrammatically in Fig. 34.

This latter reaction is rapid and complete, so that sulphur dioxide may be completely washed out of dilute gases by treating these gases with ammonium thiosulphate.

Ammonium polythionate has proven a very effective means for extracting hydrogen sulphide and ammonia, either in combination or separately, from coal gas. The intermediate reactions are many, and therefore the final ones only are given here.

The polythionate secured with the reaction given above is now treated with gas containing hydrogen sulphide and ammonia,

$$(NH_4)_2S_4O_6 + (NH_4)_2S = 2(NH_4)_2S_2O_3 + S,$$

and treating with hydrogen sulphide, we have

$$(NH_4)_2S_4O_6 + 3H_2S = (NH_4)_2S_2O_3 + 5S + 3H_2O,$$

and then treating with ammonia, we have

$$(NH_4)_2S_4O_6 + 2NH_3 + H_2O = (NH_4)_2SO_4 + (NH_4)_2S_2O_3 + S.$$

In each of these three reactions thiosulphate is formed, and this compound is again changed into polythionate by

treating the liquor with sulphur dioxide according to the first reaction, or

$$2(NH_4)_2S_2O_3 + 3SO_2 = (NH_4)_2S_4O_6 + (NH_4)_2S_3O_6.$$

By an alternate treatment of the solution with coal gas and then with sulphurous acid, the content of ammonium salts gradually increases; finally by treatment with sulphurous acid polythionates are formed which are in turn broken down by the application of heat with the resultant formation of sulphate, or

$$2(NH_4)_2S_2O_3 + 3SO_2 + S = 2(NH_4)_2S_4O_6,$$

and

$$3(NH_4)_2S_4O_6 + \triangle = 3(NH_4)_2SO_4 + 3SO_2 + S,$$

and by adding these two equations we have

$$(NH_4)_2S_4O_6 + 2(NH_4)_2S_2O_6 = 3(NH_4)_2SO_4 + 5S.$$

That is, when the content of polythionate has reached a certain maximum, the sulphurous acid which has been set free during sulphate formation is sufficient to change the thiosulphate present into polythionate and finally into ammonium sulphate. The precipitated granular sulphur can now be separated from the sulphate solution and the latter can be evaporated for the production of the ammonium sulphate salts.

This polythionate process presents a simple and reliable solution of the old problem of completely combining ammonia and sulphur in illuminating or coke-oven gas for the production of ammonium sulphate. As is seen from the reactions given above, no other oxydizing agent except atmospheric oxygen is necessary, and the latter is only used in the sulphur stove where the sulphur is burned to form sulphur dioxide, this sulphur stove thus displacing the sulphuric acid factory which has hitherto been a necessity.

The method of operation can best be understood by following the diagram (Fig. 34). The plant is started by filling the two regenerator tanks (*B*) and *C*) as well as the wash liquor tank (*D*) with weak ammonia liquor from the works, or with fresh water, this liquor or water being then

pumped into the supply tank (*U*) from whence it flows into the top of the washer (*A*). Ammonia extraction immediately follows, and the liquor flows from the bottom of the washer as thiosulphate, entering regenerator (*B*), where it is treated with sulphur dioxide coming from the sulphur stove (*F*), the sulphur dioxide being forced through the liquor due to pressure produced by the compressor (*G*). The overflow from regenerator (*B*) enters regenerator (*C*), where a further treatment with sulphur dioxide is effected, and then enters the wash liquor tank (*D*), from whence it is again pumped to the washer.

Alternately treating the liquor with sulphur dioxide and with crude gas forms polythionate in the first instance and thiosulphate in the second, the polythionate being the active washing medium; an equivalent amount of hydrogen sulphide is removed from the gas in conjunction with the ammonia in the washer.

When the liquor has obtained a strength equivalent to 35 or 40 per cent of ammonium sulphate, a portion of this concentrated solution is pumped into the oxidation or finishing tank (*H*), it being replaced in the circulating system with weak liquor from prior condensation. In the finishing tank (*H*) the polythionate liquor is treated with heat through the medium of a steam coil, and some sulphur dioxide if this should be necessary; by this treatment the thiosulphates are transformed into polythionates, which are in turn decomposed into sulphate and free sulphur.

The liquor, when decomposed, is drawn off from the finishing tank onto the sulphur drain board (*J*), and the free sulphur, which is in the form of hard grains, is placed in the centrifugal (*K*) where its moisture is expelled; this sulphur is returned to the sulphur stove (*F*) for the further production of sulphur dioxide.

The liquor from the drain board (*J*), as well as that from the centrifugal (*K*), flows to the precipitating tank (*Q*), where it is treated with some concentrated ammonia, or $(NH_4)_2S$ from the condenser (*T*); this liquor is then transferred to the storage tank (*L*) and is pumped from there to the vacuum boiler (*M*). The concentrated ammonia, or $(NH_4)_2S$, from the still and condenser is sent into the precipi-

tating tank in order that any iron held in suspension may thrown down, thus ensuring a clean, white salt; the amount ammonia used for this purpose is very small, as will be sho later, and it is all recovered in the sulphate. The liquor evaporated under a vacuum in the boiler (an open evapora may be used if desired), and the salts are drawn out onto drain board (*N*), and from thence to the centrifugal (*O*) a rotary dryer (*P*), the salts thus produced being ready bagging and shipping. All mother liquor from the dra board and centrifugal returns to tank (*L*) and is from the pumped back into the boiler.

The still (*R*) is used for the purpose of evaporating a ammonia liquor thrown down by previous condensation, th vapors being returned to the gas at the inlet to the wash a small portion of the vapor being sent into the conden (*T*) to produce the $(NH_4)_2S$ used in the precipitating ta The use of a still is dependent upon the method of operatic if Feld's system of hot-tar extraction is installed, a still v not be necessary, as there will be no precipitation of ammo under these conditions; a still is also not necessary if t production of ammonia liquor does not exceed the amount liquor required in circulation.

This process requires but very little expert control, t usual mechanics attending the machinery being capable making the necessary liquor tests after some little instructic

COMBINED BUEB CYANOGEN AND FELD SULPHATE PLANT

As stated before, ammonium sulphate is formed in the Bu process, and therefore these two systems in combination fo a very remunerative proposition. The combined plant shown in diagram in Fig. 35; the operation of both syste is the same as described for the separate processes, but t final liquor from both systems is run into a common sulpha liquor storage tank from whence it is pumped to the vacuu boiler.

Example. Three Million Cubic Foot Coal-Gas Plant: Ammonia assumed at five pounds per ton of coal carbonize or five pounds per 10,000 cubic feet of gas, equivalent to 0. pound per 100 cubic feet of gas.

Assume 25 per cent of the total ammonia removed in condensation (this amount is probably large), and as 0.05 pound is equivalent to 350 grains of ammonia per 100 cubic feet, we will have:

In condensation $350 \times 0.25 =$ say 88 grains NH_3 per 100 cu. ft.

In Plant $350 \times 0.75 =$ say 262 grains NH_3 per 100 cu. ft.

The total ammonia sent to the Cyanogen and Ammonia plant will then be:

$$262 \times 30{,}000 = 7{,}860{,}000 \text{ grains, or}$$
$$\frac{7{,}860{,}000}{7000} = 1123 \text{ pounds of } NH_3 \text{ per day.}$$

The total ammonia in the condensate will be

$$88 \times 30{,}000 = 2{,}640{,}000 \text{ grains per day, or}$$
$$\frac{2{,}640{,}000}{7000} = 377 \text{ pounds per day.}$$

If the coal produces 0.07 pound of water per pound of coal, or $2000 \times 0.07 = 140$ pounds of water per ton of coal, equivalent to $140 \times 300 = 42{,}000$ pounds of water per day, equal to 5042 gallons, and all of this water is precipitated with a content of 377 pounds of ammonia (an extreme case) this water would contain $377 \times 16 = 6032$ ounces of ammonia, and the ammonia per gallon of water would be $\frac{6032}{5042} = 1.19$ ounces, and the ounce strength of this liquor, with

$$2\,(NH_3) = 34, \text{ and} H_2\,SO_4 = 98$$

would be

$$1.19 \times \frac{98}{34} = 3.42,$$

or there will be 5042 gallons of 3.42 ounce liquor in condensate to be treated each day. All of this water does not pass off with the ammonia, some of it remaining with the tar, but for the purposes of this example, and to explain an extreme case, this fact has not been considered.

We will also assume that the gas carries 600 grains of hydrogen sulphide and 120 grains of cyanogen per 100 cubic feet.

The amount of cyanogen present in the gas will then be

$$\frac{120 \times 30{,}000}{7000} = 514 \text{ pounds per day.}$$

The amount of iron sulphate ($FeSO_4$) required per day for the absorption of this amount of cyanogen will be given by the reaction

$$2FeSO_4.7H_2O + 2H_2S + 4NH_3 = 2FeS + 2(NH_4)_2SO_4, \text{ or}$$

$$556 : 156 :: x : 514, \text{ and}$$
$$x = 1832 \text{ pounds of } FeSO_4,$$

or 76.33 pounds per hour, and with a 30 per cent solution, having a specific gravity of 1.174 and weighing 9.78 pounds per gallon, 3.565 pounds being required per pound of cyanogen, $\frac{3.565}{2.93} = 1.22$ gallons of solution will be required for each pound of cyanogen in the gas.

The amount of ammonia removed from the gas to precipitate the $FeSO_4$ as FeS will also be given by the above reaction, or

$$556 : 68 :: 1832 : x, \text{ and}$$
$$x = 224 \text{ pounds per day.}$$

The $(NH_4)_2\ Fe_2(CN)_6$ contains 11.84 per cent of ammonia, and as 514 pounds of cyanogen per day is equivalent to

$$514 \times 1.95 = 1002 \text{ pounds of } (NH_4)_2\ Fe_2\ (CN)_6,$$

we will find $1002 \times 0.1184 = 119$ pounds of ammonia present in the "blue," therefore a total of $224 + 119 = 343$ pounds of ammonia are removed from the gas each day in the cyanogen plant, of which 224 pounds are available for sulphate manufacture, being equivalent to $224 \times 3.88 = 869$ pounds of ammonium sulphate per day.

In addition to this amount of ammonium sulphate, some sulphate is also produced in the neutralizing tank by the union of $(NH_4)_2S$ with the $FeSO_4$ and the acid of this liquor, but the amount is indeterminate.

The amount of H_2S removed from the gas is equivalent to about 80 per cent of the NH_3 in practice, or $224 \times 0.80 = 179.2$ pounds, plus that due to the increased alkalinity of the sludge, which latter is variable and due to operating conditions.

The total H_2S in the gas is $30,000 \times 600 = 18,000,000$ grains, and $179.2 \times 7000 = 1,254,400$ grains are removed as shown above, leaving 16,745,600 grains still to be expelled.

The amount of sulphuric acid used per day in the cyanogen neutralizing tank is a variable quantity, it depending entirely upon the alkalinity of the liquor, but on an average it amounts to about 0.9 pound per ton of coal carbonized, or in this case to $300 \times 0.9 = 270$ pounds per day.

The amount of ammonia remaining in the gas going to the Feld plant is $1123 - 343 = 790$ pounds per day, equivalent to $790 \times 3.88 = 3065$ pounds of sulphate, and the amount of hydrogen sulphide removed here will be $790 \times 0.80 = 632$ pounds per day, equivalent to or containing $632 \times 0.94 = 594$ pounds of sulphur.

The amount of condensate ahead of the plant contains 377 pounds of ammonia per day, equivalent to $377 \times 3.88 = 1463$ pounds of sulphate.

The additional hydrogen sulphide removed by this quantity of ammonia is $377 \times 0.80 = 302$ pounds, containing $302 \times 0.94 = 284$ pounds of sulphur, making the total sulphur recovered from the gas $594 + 284 = 878$ pounds per day.

The amount of sulphur required per day to enter into combination is based upon the sulphur in the sulphate, or 0.2424 pound per pound of sulphate, and as the total sulphate produced in the Feld plant will be $3065 + 1463 = 4528$ pounds per day, $4528 \times 0.2424 = 1098$ pounds of sulphur will be required, necessitating the purchase of $1098 - 878 = 220$ pounds of sulphur per day.

This combined plant saves quite an amount of iron in the oxide contained in the purifiers, as seen below:

Total H_2S in gas $= \frac{18,000,000}{7000} = 2572$ pounds per day, while the total H_2S removed is $179.2 + 632 + 302 = 1113.2$ pounds per day, and the cyanogen removed amounts to 514 pounds.

Fe required in the purifiers for the total elimination of $(CN)_2$ and H_2S contained in the gas is

For $H_2S = 2572 \times 1.56 = 4012$ pounds
For $(CN)_2 = 514 \times 1.19 = 612$ "
Total Fe $= 4624$ pounds per day.

Fe saved by the removal of H_2S and $(CN)_2$ in the combined plant is

For	H_2S = 1113.2	× 1.56 =	1737 pounds
For	$(CN)_2$ = 514	× 1.19 =	612 "
	Total Fe Saved		2349 pounds per day and

the purifier saving will amount to $= \frac{2349}{4624} = 50.8$ per cent.

It is safe to predict that the future development of the Feld process will soon present the means of entirely removing the hydrogen sulphide from the gas, thus obviating the use of purifiers with a consequent saving in labor as well as in ground space occupied.

Summarizing the above, the net income to be expected from this combined plant will be given by:

GROSS INCOME

Cyanogen per day	514 lbs. at	13.25¢ =	$ 68.10
Sulphate " "	5397 " "	3.00¢ =	161.91
NH_3 in $(CN)_2$ Cake per day	119 " "	7.00¢	8.33
Total Gross Earnings			$238.34

OPERATING EXPENSES

$FeSO_4$	per day 1832	lbs. at	$ 9.50	per ton =	$ 8.70
H_2SO_4	" " 270	" "	11.50	" " =	1.55
Sulphur	" " 220	" "	22.00	" " =	2.53
Steam	" " 33.2	M. lbs. at	20¢	" M. =	6.64
Power	" " 1075	K.W.H. at	1¢	=	10.75
Lime	" " 470	lbs. at	$8.50	" ton =	2.00
Oil, Waste, Miscellaneous, Repairs					4.00
Labor					10.00
Total Operating Expense					= $46.27

Gross Income per day	$238.34
Operating Expense per day	46.17
Net Income per day	$192.17

or with 250 maximum working days, $192.17 × 250 = $48,042.50 per year.

While these figures can be used as a guide, the units should be corrected to suit locations and cost of supplies.

As stated before, the content of cyanogen and ammonia in coal gas is dependent upon the kind of coal used, the type of carbonizing chamber, and the conditions under which carbonization is effected, especially with reference to heats, length of carbonization period, size of charge, and the amount of seal carried in the hydraulic main, and it should be the object of every operator to remove the gas from the retort as quickly as possible in order to produce a large yield of ammonia; the usual temperatures of carbonization so closely approach the dissociation temperature of ammonia, that protracted contact with the incandescent coke in the retort is liable to break down some of the ammonia already formed and thus reduce the maximum yield.

The following tests were made to determine the cyanogen and ammonia content at various temperatures in a plant where cyanogen is extracted by the Bueb process and where the Feld sulphate recovery system is used, this plant being equipped with both horizontal and inclined retorts, operating with a little more than one inch seal on the hydraulic main.

An average of ten tests on the gas leaving the hydraulic main showed that at 143° F. there were 352.4 grains of ammonia per 100 cubic feet of gas from the inclined retorts, and the gas from the horizontal retorts contained 358 grains per 100 cubic feet at 135° F.

Simultaneous tests made at the outlet of the first cooler, for the purpose of determining the amount of ammonia removed by cooling for each degree Fahrenheit showed that at 104° F. the same gas contained 284 grains per 100 cubic feet, or it had sustained a loss of 1.85 grains per 100 cubic feet for each degree in the reduction of temperature, and the ammonia removed with the tar at these points ranged from 1 to 3 per cent of the total content of the gas.

The factor of 1.85 was used on gas between 100° F. and 150° F., and by correction the gas at 150° F. contained 365 grains of ammonia per 100 cubic feet from the inclined retorts, and 385 grains from the horizontal retorts.

The cyanogen content of the gas at 146° F. was 129 grains per 100 cubic feet, and there was practically no reduction in this content due to a reduction in temperature.

In examining into the operating conditions of the combined

Bueb and Feld plant just described, 365 grains of ammonia and 130 grains of cyanogen will therefore be assumed in place of the amounts previously mentioned. There is absolutely no difficulty in removing 100 per cent of ammonia, but the hydrogen sulphide extraction will depend upon the excess of polythionates over thiosulphates in the wash liquor, or on the excess of polythionates over what is required to entirely remove the ammonia.

Under these conditions we will have

I. NH_3 in gas at inlet to tar washer:

$$\frac{30{,}000 \times 365}{7000} = 1564.3 \text{ pounds at } 150° \text{ F.}$$

II. NH_3 in gas at inlet to naphthalene washer, assuming that a naphthalene washer is interposed between the tar and cyanogen washer, and assuming that 5 per cent of ammonia would be removed with the tar, there would be at this point:

$$1564.3 - (1564.3 \times 0.05) = 1486 \text{ pounds at } 147° \text{ F.}$$

III. NH_3 in gas at inlet to cyanogen washer: Allowing a drop in temperature of 5 degrees in the pipe connections between No. I and No. III, the ammonia in the gas at this point would be 1446 pounds at 145° F.

At 145° F., and with an average cyanogen content of 130 grains per 100 cubic feet, the amount of cyanogen in the gas would be

$$\frac{130 \times 30{,}000}{7000} = 557 \text{ pounds per day,}$$

and as one pound of cyanogen will remove 0.665 pound of ammonia, $557 \times 0.665 = 370$ pounds of ammonia per day, or $\frac{370}{1.446} = 25.5$ per cent of the total ammonia will be removed in the cyanogen washer.

About one-third, or 123 pounds of this ammonia exists as combined ammonia in the " blue," the remaining 247 pounds being available as ammonium sulphate, providing the cyanogen cake is thoroughly washed in the cake wash tanks, thus removing all sulphate liquor from the combination. A summary of the above contents is given in Table XVII.

TABLE XVII. — AMMONIA CONTENT

Location	Temp. of gas in degrees F.	Ammonia	
		Gr. per 100	Lbs. per day
I. Inlet to tar washer	150	365	1564.3
II. Inlet to naphthalene washer	147	347	1486.0
III. Inlet to cyanogen washer	145	337	1446.0
IV. Inlet to polythionate washer	145	251	1076.0

As shown by the reactions, one pound of cyanogen will require 3.565 pounds of copperas for its complete removal, or there will be required

$$557 \times 3.565 = 1986 \text{ pounds of } FeSO_4.7H_2O,$$

and in terms of a 30 per cent solution, with a specific gravity of 1.174, there will be required

$$\frac{1986}{2.93 \times 24} = 28 \text{ gallons per hour.}$$

Calculating to a 25 per cent cyanogen press cake, there will be $557 \times 4 = 2228$ pounds of press cake per day, or $\frac{2228}{300} = 7.43$ pounds of cake per ton of coal.

Figuring the liquor as 70 per cent of the total used, there would be $677 \times 0.70 = 474$ gallons of press liquor per day, this liquor containing $\frac{958}{474} = 2$ pounds of sulphate per gallon, and the amount of ammonia at the outlet of the cyanogen washer would be $1446 - 370 = 1076$ pounds per day, or 251 grains per 100 cubic feet.

In actual practice the amount of ammonia removed in the cyanogen washer is higher than the theoretical 25.5 per cent as calculated, for owing to variations in the volume of gas produced at various times, and also the possibility of a change in the cyanogen content of the gas, it is next to impossible to

regulate the supply of wash liquor to take care c changes.

For instance, if the liquor supply per hour to the c washer is regulated to treat 125,000 cubic feet of gas cyanogen content of 130 grains per 100 cubic feet, a 115,000 cubic feet of gas is actually treated, there w excess ammonia removed from the gas, as each pound peras in excess of what is required to combine with the gen will remove 0.44 pound of ammonia, but this amr available as sulphate in the resultant liquor.

The amount of sulphate recovered from the cyanoger will depend entirely upon the amount of washing tc the press cake is subjected, and while the ammonia of the cake is paid for as such, it is worth more as s than as ammonia.

The amount of sulphuric acid required in the neu will depend upon the free ammonia and the iron s present in the cyanogen sludge in excess of what is r to combine with the cyanogen.

However, these questions of excess ammonia remov increased sulphuric acid consumption depend entirel liquor regulation, and by working to a fixed percen cyanogen removal, say 95 per cent, instead of compl traction, there should be no difficulty in solving problems.

In the polythionate process, based on sulphate r and in terms of a 35 per cent liquor, there will, wit pounds of ammonia, or 251 grains per 100 cubic feet, l duced each day

$1076 \times 3.88 = 4175$ pounds of sulphate, or in terms o per cent liquor with a specific gravity of 1.20,

$$\frac{4175}{3.5} = 1193 \text{ gallons per day,}$$

to which must be added the 474 gallons of press liquc taining two pounds of sulphate per gallon.

The amount of liquor in circulation depends upc nature of the compounds present in the liquor, and tl turn upon the degree of regeneration of thiosulphat polythionate, because ammonium thiosulphate, $(NH_4$ will remove ammonia but no hydrogen sulphide, ar

purification efficiency of thiosulphate and polythionate can be obtained from the following equations:

I. $(NH_4)_2S_2O_3 + 2NH_3 + 2H_2O = (NH_4)_2SO_4 + (NH_4)_2S +$

H_2O, or one pound of $(NH_4)_2S_2O_3$ will remove 0.23 pound of ammonia.

II. $(NH_4)_2S_4O_6 + 2NH_3 + H_2S = 2(NH_4)_2S_2O_3 + S$ (A)

$(NH_4)_2S_2O_3 + 2NH_3 + 2H_2O = (NH_4)_2S + (NH_4)_2SO_4 + H_2O$ (B)

Due to this double decomposition, one pound of $(NH_4)_2S_4O_6$ will remove 0.39 pound of ammonia.

At a European Plant, one where the Feld system was first installed, the liquor with a specific gravity of 1.25 contained:
$(NH_4)_2S_2O_3$...7.5 molecules, or 5.55 per cent, or 0.57 pound of ammonium thiosulphate per gallon,
$(NH_4)_2S_4O_6$...4.0 molecules, or 2.60 per cent, or 0.27 pound of ammonium tetrathionate per gallon, or the thiosulphate was to the polythionate as 7.5: 4, and one gallon of this liquor would remove $0.57 \times 0.23 = 0.131$ pound of NH_3, and

$0.27 \times 0.39 = 0.105$ " " " or

a total of $0.131 + 0.105 = 0.236$ pound of ammonia, and one pound of ammonia under these conditions would require $\frac{1}{0.236} = 4.24$ gallons of liquor; therefore, for the amount of ammonia present in the above described plant,

$1076 \times 4.24 = 4562$ gallons, or

190 gallons per hour,

3.17 gallons per minute,

equivalent to 1.52 gallons of liquor of this composition in circulation per 1000 cubic feet of gas.

If the above liquor, which contains 31.08 per cent $(NH_4)_2SO_4$, or 8.02 per cent NH_3, and 20 per cent of which is composed of thiosulphate and tetrathionate compounds, had this 20 per cent existing as all tetrathionate, then one gallon of 1.25 specific gravity liquor would contain 12.3 per cent $(NH_4)_2S_4O_6$, equivalent to 1.28 pounds of tetrathionate, and it would remove 0.5 pound of ammonia, thus only two gallons of liquor of this composition would be required in circulation per pound of ammonia.

The ratio of polythionate to thiosulphate is dependent upon regeneration, or upon an emulsion with sulphur dioxide produced by the burning of sulphur, and a better ratio than 7.5 to 4 will ensure better extraction, and if the tankage is arranged for the 7.5 to 4 ratio and the liquor is treated with more SO_2 than this ratio requires, the regenerating reactions will progress much slower, owing to the increased capacity of the vessels, and they will therefore be more complete.

The amount of sulphur to be burned is obtained from the following regeneration reactions:

III. $2(NH_4)_2S + 3SO_2 = 2(NH_4)_2S_2O_3 + S.$

IV. $2(NH_4)_2S_2O_3 + 3SO_2 + S = 2(NH_4)_2S_4O_6,$

and calculating from this we find that one pound of thiosulphate requires 0.32 pound of sulphur; then 4562 gallons of liquor containing 0.57 pound of thiosulphate per gallon, and 0.27 pound of polythionate per gallon, will require the combustion of

$(4562 \times 0.57)\ 0.32 =$ 832 pounds of sulphur,
$(4562 \times 0.27)\ 0.73 =$ 899 " " "
or a total of 1731 pounds of sulphur per day

for the regeneration of this amount of liquor, or $\frac{1731}{1076} = 1.61$ pounds of sulphur per pound of ammonia in the gas.

If the liquor had been so regenerated that the entire 20 per cent of thiosulphate and polythionate compounds had been converted into polythionate requiring two gallons of liquor per pound of ammonia, or $1076 \times 2 = 2152$ gallons per day containing $2152 \times 1.28 = 2755$ pounds of $(NH_4)_2S_4O_6$, and when reduced as per the above reactions, there would be required to regenerate $2755 \times 0.73 = 2011$ pounds of sulphur therefore to obtain the same extraction results, as regards ammonia, with this liquor it would be necessary to burn 280 pounds, or slightly over 16 per cent more sulphur than would be required to regenerate the 7.5 to 4 liquor.

From the efficiency ratio of polythionate to thiosulphate which is

	S_4O_6 : S_2O_3
For ammonia	1.7 : 1.0
For hydrogen sulphide	1.0 : 0.0,

it is readily seen that a higher hydrogen sulphide extraction will be obtained when the liquor contains a higher percentage of $(NH_4)_2S_4O_6$ than is given in the 7.5 to 4 ratio, and this can readily be secured by burning the proper quantity of sulphur.

As stated before, the only oxidizing agent used during the process is air, and this is used to maintain combustion in the sulphur burner. One pound of sulphur requires one pound of oxygen, or 4.315 pounds of air, or $4.315 \times 13.06 = 56.3$ cubic feet of air per pound of sulphur; this would require in the first case $1731 \times 56.3 = 97{,}455$ cubic feet of air per day, or 68 cubic feet per minute, and in the second case $2011 \times 56.3 = 113{,}219$ cubic feet per day, or 80 cubic feet per minute, and for the production of a 10 per cent SO_2 double this quantity, or 136 and 160 cubic feet respectively will be required per minute, and an excess of air is an undoubted advantage and aid to regeneration due to greater liquor agitation.

The sulphur thus burned is not lost, but it is all, with the exception of the small amount which may be required to complete the sulphate combination, recovered in the finishing tank, from whence it is returned to the sulphur stove.

The amount of ammonia required to precipitate the iron in the 1667 gallons of liquor is small. If this finished liquor weighs nine pounds per gallon, giving a total of 15,003 pounds of liquor, and assuming the maximum Fe content of this liquor to be one-quarter of 1 per cent, the amount of Fe to be precipitated will be $15{,}003 \times 0.0025 = 37.5$ pounds.

One pound of Fe requires 0.1225 pound of ammonia for its precipitation, or the amount of ammonia required will be $37.5 \times 0.1225 = 4.59$ pounds per day, and if liquor containing 1.54 per cent of NH_3 is used for this purpose, or liquor containing $8.33 \times 0.0154 = 0.13$ pound of NH_3, the amount to be evaporated per day will be $\frac{4.59}{0.13} = 35.3$ gallons.

Some of the Feld plants being built at present are designed to operate under a vacuum instead of a pressure, in which case the compressor is replaced by an exhauster and the sulphur dioxide is drawn through the liquor instead of being pressed through as explained above.

As the Feld system of purification is but little known in the United States, it may be well to mention that two plants, each of 3,000,000 cubic feet capacity, are being built in the

United States at present, one of them being for the production of ammonium sulphate only, by the Feld process, the other being a combination between the Bueb Cyanogen and the Feld Sulphate systems, as described in the preceding pages.

Among the larger Feld plants being erected in Europe at the present time may be mentioned:

One in France for the direct recovery of by-products from 1250 tons of coal per day.

One in Germany for 1600 tons of coal per day.

One for the production of 5.5 tons of sulphate per day from producer gas.

One for the purification of 5,500,000 cubic feet of coal gas with sulphate production.

One for the production of pitch and oils from 800 tons of coal per day.

The *Feld Direct Sulphate Plant* as built in the United States differs radically from that previously described, in that the European system is operated under pressure, while that in America operates under a partial vacuum, as shown in diagram on Fig. 35a.

The gas is passed through two washers in series, the fresh wash liquor from the regulating tank being admitted to the top of the second washer, overflowing from there to the process tank located on the lower floor; a centrifugal pump takes this liquor from the process tank and pumps it up to the supply tank over the first washer, this washer being fed from this supply tank.

The liquor from the process tank under the first washer is pumped up into the V-shaped supply tank, running from there through a sight-overflow into the bottom of the mixing tank; the liquor now flows from the top of this mixing tank through the second and first acidifiers in the direction indicated.

The sulphur is burned to sulphur dioxide in the rotary sulphur burner, this gas passing through a sulphur melter into an all cast-iron condenser and from there up to the first acidifier, that portion of the SO_2 gas not absorbed in the first acidifier is taken up in the second, the two acidifiers and the mixing tank being kept under a partial vacuum by means of the exhauster located on the second floor.

After the liquor contains its burden of ammonium sulphate, 25 per cent is withdrawn from this train and run into the boiling tank, where it is heated by indirect steam, and where some SO_2 is added. After the polythionates have thus been broken down, the ammonium sulphate liquor, with granular sulphur in suspension, is drawn off and enters the settling tank on the second floor; any sulphur which does not drop out in this tank will be removed in the sulphur centrifugal. This sulphur is dried and then passed to the sulphur melter, where it is melted, cast into sticks, and again charged into the rotary sulphur burner.

The sulphate liquor from the centrifugal is run into the precipitating tank, where any iron which might discolor the salt is precipitated by strong ammonia liquor produced in the ammonia still. The sulphate liquor is now cleared and decanted in the three clear liquor tanks, and then pumped up to the evaporator where the salt is formed, this finished salt being then dried in the sulphate centrifugal, all mother liquor from the evaporator and centrifugal returning to the precipitating tank.

The sludge which finally collects in the precipitating tank is filter-pressed, the cake being added to the oxide in the purifiers, the clear liquor returning to the precipitator.

The plant is provided with an ammonia still to take care of any ammonia which may come down in condensation prior to the process proper, the strong liquor produced in this still being run into the first acidifier, where it joins the polythionate liquor in circulation and makes up for the liquor removed to the boiling tank.

The chemistry of the process is the same as that previously described, but the apparatus differs in many essential particulars. The difficulty of perfect operation could heretofore be traced back to the regeneration train, as the regeneration of the liquor with SO_2 gas was difficult to secure with the apparatus previously used, but the new design of vacuum acidifiers and mixers has removed this difficulty, and the contact between liquor and SO_2 gas is now practically perfect.

At the large scale experimental station, treating 1,500,000 cubic feet of gas per day, as high as 132 grains of hydrogen sulphide per 100 grains of ammonia were removed, while only an equivalent of 100 grains of H_2S per 100 grains of NH_3 are required for the sulphate combination; the ammonia was en-

tirely removed from the gas, this removal averaging 100 per cent during the entire operating period of one year. The sulphate produced was clean and white, and contained 25.7 per cent of NH_3 on the dry basis.

The improved plant recently completed at another point will shortly be placed in operation, and the results expected from there should exceed anything done at the experimental plant.

CONCLUSIONS

As seen from the system just described, the old, or indirect process required *a priori* cooling of the gas with practically a complete absorption of ammonia in water, this latter liquor being treated with steam and lime in a still and the ammonia vapors thus produced sent into a saturator, while the so-called "direct" or "semi-direct" systems, besides calling for a complete elimination of the tar, require that the temperature in the saturator be sufficiently high to prevent condensation with a consequent dilution of the acid bath.

In the Brunck system the tar-free gas was supposed to have a temperature sufficiently high to pass through the saturator without condensation, but this temperature, in spite of the fact that it was above the critical point, and notwithstanding the additional heat produced by the reaction in the acid bath, dropped with consequent condensation. Owing to the fact that an artificial increase in temperature above that of the entering gas had a bad effect upon tar recovery, this method, which at first had seemed so promising, found but little application.

The Otto process proved to be a successful endeavor to improve upon what Brunck had accomplished; Otto replaced Brunck's tar washer with liquid tar injectors of the atomizing type followed by a Pelouze drum, the latter apparatus being placed on the suction side of the exhauster. The Koppers system starts with radical condensation, thus precluding condensation in the saturator, the gas being admitted into the acid bath at a lower temperature than in the Otto, this gas being, however, heated to the required temperature by means of hot raw gas coming from the hydraulic main. Koppers distills the condensed ammonia, but the vapors are not permitted to enter the saturator immediately, as in the Mont-Cenis system, they being mixed with the gases prior to entering the saturator.

All of these processes, except the indirect, require the passing of the gas through the acid bath, producing a back pressure which is very high, as it depends upon the depth of the liquid bath, the report made by C. Heck to the German Coke Commission stating that these back pressures are 900 mm. = 35½ inches in the Otto system, and 750 mm. = 29½ inches in the Koppers system, but greater back pressures than these have been known, and it is a known fact that the power required to force a thousand cubic feet of gas through a given depth of liquid rapidly increases with this depth.

It should also be remembered that the gas in rising through the liquid of a certain height causes the useful effect of contact to decrease quickly, owing to the fact that a number of the smaller gas bubbles rapidly unite to form larger ones, thus reducing surface contact.

Charles Berthelot, in the "Revue de Metallurgie," states that it is difficult to obtain complete absorption by this acid bath, and that it is necessary to renew the surfaces of contact between the gas and the acid as often as possible; he also states that Otto does this by violent agitation of the liquid by means of a pump, thus making it possible for him to adopt a lesser travel of the gas through the acid; in contradistinction to this, it is seen that in the Mont-Cenis system a layer of tar is used on the surface of the acid in the saturator in order to prevent this very agitation.

Berthelot also states that "from experiments made it would seem that the ammonia lost due to direct sulphatation in the acid bath would be about 77 grains per ton of coal, but that this is not found to be the case in actual practice." He states that in the semi-direct process 6.8 per cent of the total ammonia is retained in the tar, and that this loss cannot occur in the indirect system because there the water which is condensed with the tar in the mains dissolves out almost the whole of the fixed salts, and that the loss in ammonia in both the direct and semi-direct acid bath systems is practically the same.

He states that a serious objection to the adoption of these direct systems is due to the presence of ammonium chloride in the gas, the difficulties produced by this constituent being due to its method of travel. A portion of this salt remains in the tar and not only occasions ammonia loss, but also causes

serious trouble due to its decomposition when distilled. The only way in which this loss can be avoided is to wash the tar with water and then to distill this water to recover the ammonia.

Further, he claims that the ammonium chloride also enters the saturator and is there decomposed by the sulphuric acid, causing a loss of heat and producing hydrochloric acid, which seriously attacks all iron work in the apparatus following the saturator unless the gas is kept alkaline, in which latter case more ammonia is lost. A portion of the ammonium chloride is always dissolved without decomposition in the bath, and the salt thus produced loses some of its fertilizer properties.

Berthelot states that the loss of ammonia per ton of coal amounts to:

Old, or indirect system	385 grains
Semi-direct system	231 "
Direct system	185 "

and that if one ton of coal produces 3000 grammes, equivalent to 6 pounds of ammonia, these losses will be

Old, or indirect system	0.84 per cent
Semi-direct system	0.50 " "
Direct system	0.40 " "

The Feld system was offered with the endeavor to overcome all of the objections given against the acid bath process, and as the former is one of chemical absorption without the use of external acid, it has successfully met a great many of the demands which would remove the troubles due to the saturator. If Feld's system of hot-tar extraction is included in the process there will be no condensation, and the gas reaches the polythionate washers containing all of its ammonia. Besides this, the cost of production plays an important rôle in the manufacture of any product, and in order to show what may be expected from the various systems reference should be made to Table XVIII, which shows the cost of sulphate manufacture by the Indirect, Semi-direct, and Direct methods as reported to the German Coke Commission by C. Heck,[1] and to which has been added the corresponding figures for the Feld system. This table shows the differences in the cost of producing one ton of sulphate by the four systems in use, and, as stated before, syn-

[1] See "Stahl und Eisen," Vol. 33, 1913.

TABLE XVIII. — ECONOMIC BALANCE FOR THE PRODUCTION OF $(NH_4)_2SO_4$ FROM 100 COKE-OVENS

	Items	Indirect	Semi-Direct	Direct	Feld
A	Coal carbonized, tons per hour	33.3	33.3	33.3	33.3
B	NH_3 liquor to be treated, tons per hr.	12	6	0.3	0.3
C	1 Exhauster power back pressure in mm. of water,	500	750	900	150
	Horse power required	39	58	70	12
	2 Horse power cold water pumps	12	12	12	12
	3 " " spray cleaners, washers, circulating pumps	..	..	5	40
	4 " " tar and ammonia pumps	7	3	2	2
	5 " " centrifugals, average per hr.	3	3	3	3
C	6 total horse power required	61	76	92	69
D	1 Steam for NH_3 Still (250 kg/cbm) tons p. hr.	3	1.5	0.075	0.075
	2 Steam for heating gas & liquor	..	0.1	0.025	..
	3 Steam for ejectors & heating	0.05	0.05	0.050	0.050
D	4 Total steam, required	3.05	1.65	0.150	0.125
	Value of power and steam consumed.				
E	Case I — Electric motive power and fresh steam for heating and distilling; for comparison, and in view of losses, take 1 H.P. at point of consumption = 1 K.W. at switchboard, or 7 kg. steam at turbo-generator, then				
	1 Steam for motive power, tons per hour	0.427	0.532	0.644	0.483
	2 Steam for heating, tons per hour	3.050	1.650	0.150	1.500
	3 Total steam, tons per hour	3.477	2.182	0.794	1.983
	4 Value of steam at 2 M per ton, M per hour	6.954	4.364	1.588	3.966
E	5 or M per year	60,900	38,100	13,900	34,800
F	Case II — Using exhaust steam for power production in steam turbines.				
	1 Steam for heating, etc., tons per hour	3.05	1.65	0.150	0.125
	2 With 25 kg. steam p. H. P. the power to be derived from this quantity is	120	66	6	5
	3 Remaining for electric power H. P.	..	10	86	64
	4 Equivalent to, tons per hour	..	0.07	0.602	0.448
	5 Total steam tons per hour	3.050	1.720	0.752	0.573
	6 Value of steam at 2 M per ton, M per hour	6.100	3.440	1.504	1.146
F	7 of M per year	53,400	31,000	13,150	10,050
G	1 Cooling water required (1 cbm = 0.08M) M. per year	8,400	4,200	..	..
	2 Sulphuric acid required (1 cbm = 30.00M) "	105,000	105,000	105,000	..
	3 Lime required (1 ton = 15.00M) "	2,200	1,100	500	500
	4 Sulphur required (1 ton = 92.00M) "	..	..	..	11,600
	5 Miscellaneous "	3,500	3,500	3,500	3,500
G	5 Total material used, M per year	119,100	113,800	109,000	15,600
H	1 Salaries and labor, M per year	35,000	35,000	35,000	35,000
J	1 Cost of operation, case 1 M per year	215,000	186,900	157,900	85,400
K	1 Cost of operation, case II M per year	207,500	179,800	157,150	60,650
L	1 Sulphate produced, 25 lbs. per ton, tons per year.	3,320	3,320	3,320	3,320
M	1 Cost per ton of sulphate, case I	$16.25	$14.08	$11.89	$6.50
N	1 Cost per ton of sulphate, case II	$15.65	$13.54	$11.84	$4.57

thetic ammonia will affect the market wherever power is cheap enough to permit of its production; therefore the gas producer should closely examine into all existing conditions before determining upon which system is best to install. While the cost figures given are all theoretical, the same error will probably apply in practice to all four systems, but the elimination of purchased sulphuric acid in the Feld process reduces the ultimate cost at once by the value of this constituent of sulphate.

Diagram III is a graphic representation of the principal acid bath systems, showing the usual operating temperatures for comparison.

Before closing the chapter on ammonia it will be well, under present circumstances, to call attention to the manufacture of nitric acid from ammonia, the conversion process being commonly known as the "Ostwald," although there are quite a number of such processes which operate on the same principle, but which differ in the design of the apparatus as well as in the character of the catalyzer used.

The conduct of the present war will require a vast amount of nitric acid, and although export from the natural saltpeter fields of Chile is still open, political changes may close this field to us at any time, and we would then perforce be obliged to turn to atmospheric fixation of nitrogen, or some process similar to the Ostwald to supply our pressing demands.

The fixation of atmospheric nitrogen is limited to such localities where cheap electric power is available, and therefore, the Ostwald process lends itself to operations in various fields where sufficient electric power at low cost is not obtainable. Extensive data on the Ostwald process cannot be secured at present, and although it has been reported that this process is in extensive use in Germany, the operators are very careful as to any information which might point to its success.

In 1900 Ostwald took up the study of the oxidation of ammonia, and he soon discovered the conditions under which the reaction proceeded; in the laboratory he was able to obtain a yield of over 85 per cent of HNO on the ammonia. He established the fact that platinized platinum, or smooth platinum roughened by depositing a thin layer of platinum sponge on its surface, was the best catalyzer, and that a thin layer of the catalyst could be worked to better advantage than a thick one;

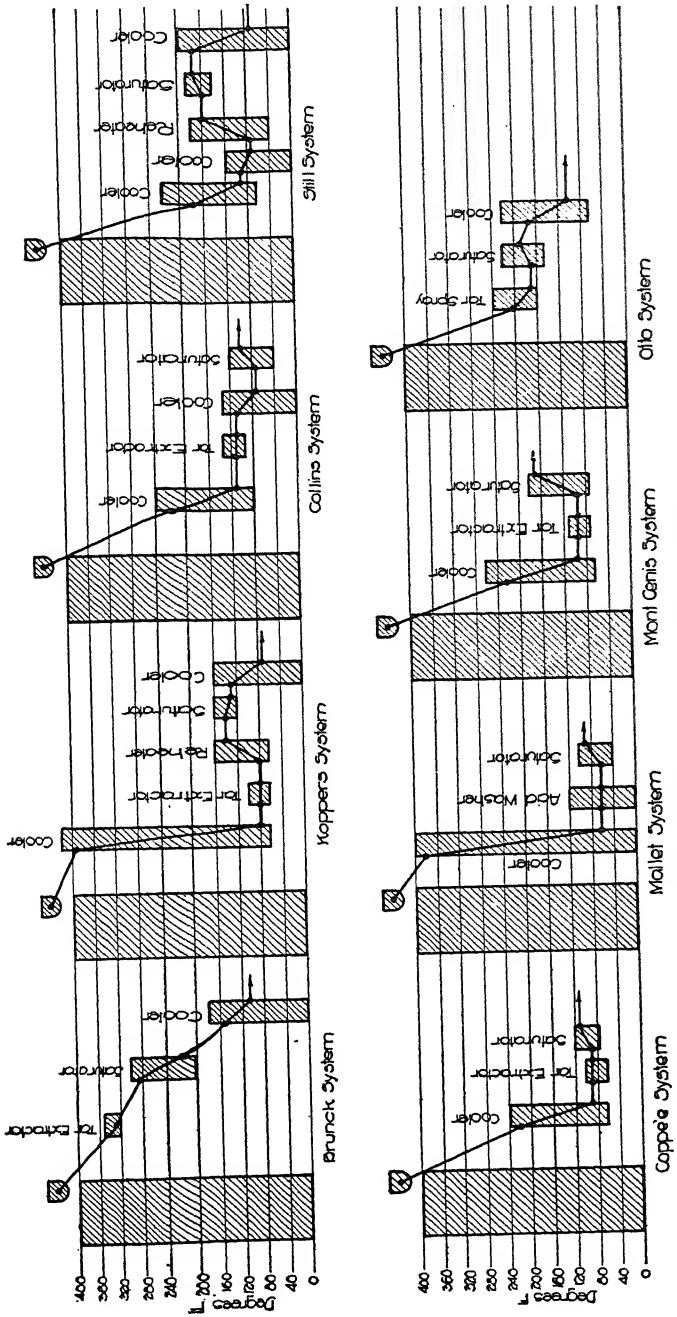


Diagram III.—Operating Temperatures, Acid Bath Systems.

also that the gas mixture must be caused to pass over the catalyst at a high velocity.

A factory was built at Gerthe, near Bochum in 1909, and it is stated that this plant had an annual production of 2400 tons of 53 per cent nitric acid, using ammonia derived from the carbonization of coal. Another report covering this plant states that it produces 2000 tons of ammonium nitrate per year.

This process was purchased by the Nitrates Products Company, Ltd., London, in 1910, the new company taking over the Gerthe plant, and erecting a new plant at Vilvorde, Belgium, the latter plant producing 40 to 50 per cent nitric acid.

The original converters[1] were constructed in such manner that an exchange of heat occurred between the incoming and the outgoing gas, thus not only keeping the catalyzer at the proper temperature of 572° F., because of the strongly exothermic character of the reaction $NH_3 + 2O_2 = HNO_3 + H_2O$, in which 385 B. T. U. are evolved, but also serving to regulate this temperature, although considerable variation in the rate of gas flow might exist. The thickness of the catalyzer element, as well as the velocity of the gas, is so chosen that the time of contact between the two does not exceed one-hundredth of a second.

The proportion between ammonia and air can be varied considerably; an excess of ammonia gives ammonium nitrate as the end product, while if the ammonia and the air are so proportioned that the equation $NH_3 + 2O_2 = HNO_3 + H_2O$ is fulfilled, and no water is dripped on the absorption towers, the maximum strength of nitric acid theoretically obtainable will be 77.8 per cent. Ostwald states that no less air should be used than represented by the equation $2NH_3 + 7O = 2NO_2 + 3H_2O$, but in this case a very rapid passage of the gas will result in obtaining a mixture of ammonium nitrate and ammonium nitrite in the exit gases.

Camille Matignon states that the above reactions are not entirely correct, as at the temperature of the reaction neither NO_2 nor HNO_3 can exist, and that the equation should be written $2NH_3 + 5O = 2NO + 3H_2O$. It is of course understood that if an excess of air is used the NO will quickly oxidize

[1] F. C. Zeisberg. "Met. Chem. Engrg." Vol. XV. Page 300.

to NO_2 as soon as the temperature is sufficiently reduced. The process of oxidation begins as soon as the temperature drops below 1112° F., but it cannot become complete until the temperature drops to 284° F.

At this lower temperature, moreover, the reaction velocity is very low, so that an appreciable time must elapse before the reaction becomes complete.

"Metall und Erz," 1916, Vol. XIII, page 21, published a diagram of a converter, the catalyzer in this apparatus being platinum gauze electrically heated to 1292° F. The gases enter at the bottom and pass upward through the gauze, no heat exchange being effected. At this temperature the conversion is almost quantitative, steam and nitric oxide (NO) being the end products, which would indicate that the equation of reaction is $4NH_3 + 5O_2 = 4NO + 6H_2O$.

To keep the gauze heated, electricity is supplied at 25 volts and 135 amp., or 3.375 kw. The article mentioned does not give the capacity of a converter, but from the description of the ammonia gas purifying apparatus, Zeisberg assumes that three converters handle from 275 to 2750 pounds of NH_3 per day, hence one converter can handle about 528 pounds per day, or 22 pounds per hour. At a conversion efficiency of 85 per cent, 10 pounds of NH_3 will produce 31.5 pounds of HNO_3, and 100 pounds of HNO_3 will therefore require 4.9 K.W.H. to maintain the temperature in the catalyzer.

The amount of platinum required to effect the conversion is about 329 grains per 100 pounds of HNO_3 per 24 hours, and the elements are renewed once a month.

The converters are constructed of iron up to the contact element, and beyond this of iron lined with aluminum; at a point far enough away from the converter for condensation to occur, the gas lines must be made of an acid-resisting material, such as chemical ware. Ostwald states that nickel steel is not attacked by hot nitrous gases, and can therefore be used in place of the aluminum-lined iron.

One design of plant embracing the Ostwald process is shown diagramatically in Fig. 35b, the catalyzer being of a type devised by Frank and Caro. The ammonia is purified by distillation in the still (7) and washed in the lime washers (8), the gas passing from these washers to the ammonia and air

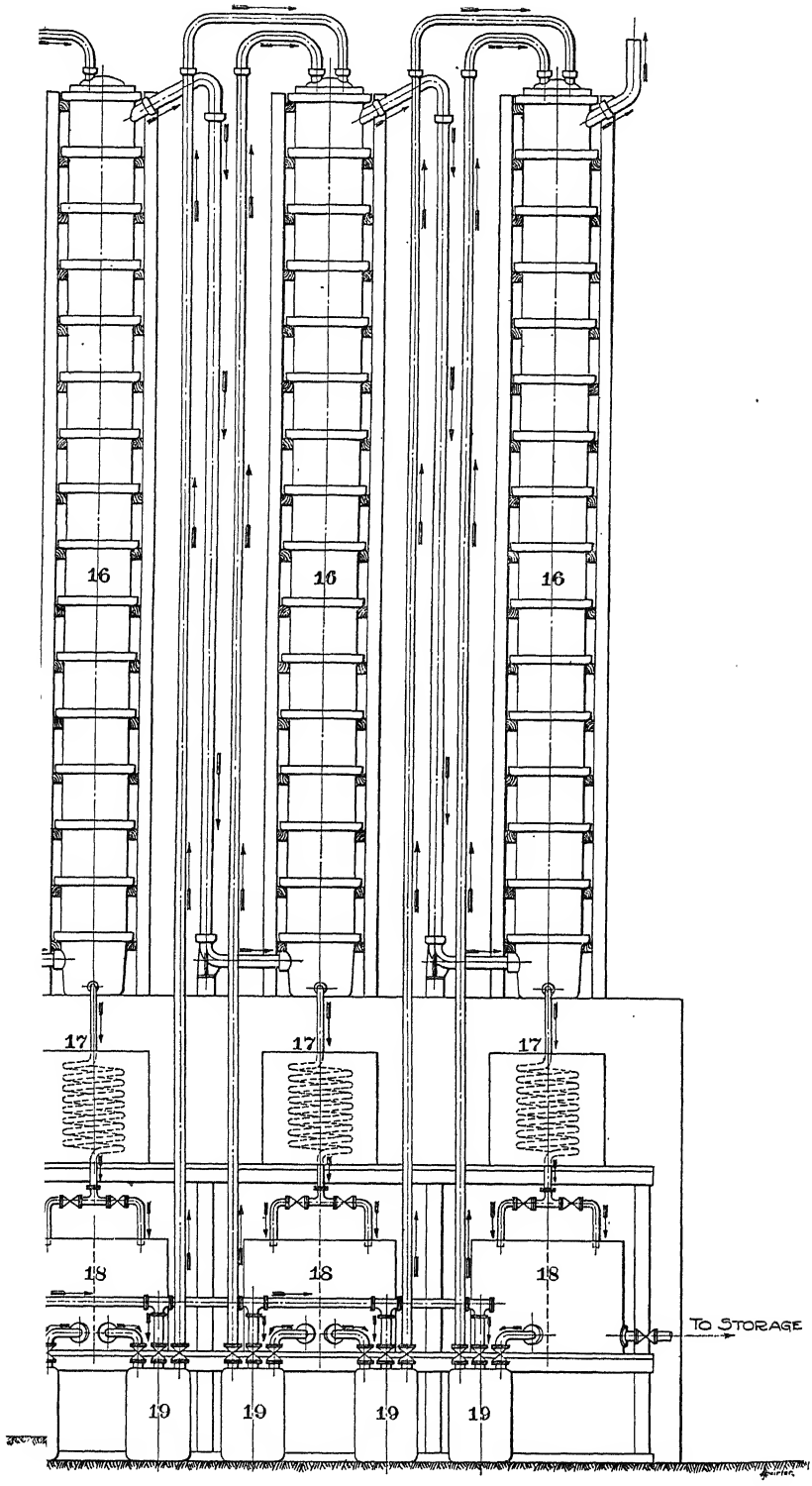
mixer (12), a container for the ammonia gas, not shown in the figure, being interposed between the ammonia-purifying plant and the mixer. Air is supplied to the ammonia through the blower (11), the properly proportioned mixture of air and ammonia then entering the catalyzers (13). From the catalyzers the nitrous oxide is led to the absorbing towers (16), where it meets with a large cooling surface covered with nitric acid, which continuously trickles down and through the stone filling of the tower. The nitric acid and the water formed during the reaction are both condensed in the tower to liquid nitric acid, and any other of the higher oxides of nitrogen which may have been produced are thus given an opportunity to further oxidize and to come in contact with sufficient water to form nitric acid. The nitric acid in the towers is used repeatedly, until the proper degree of concentration is reached, all acid flowing from the towers being cooled in the condensers (17) and returned from the storage (18) through the blow tanks (19) to the top of the towers.

A coal-gas plant carbonizing 500 tons of coal per day will produce $500 \times 5 = 2500$ pounds of NH_3 per day, or 75,000 pounds per month. As one pound of NH_3 contains 0.824 pound of N, this amount of ammonia will give 61,800 pounds of N per month, and at an 85 per cent conversion we will secure

$$\frac{61{,}800 \times 0.85 \times 4.5}{2{,}000} = 118$$ tons of absolute nitric acid per month. A conversion of 85 per cent has been questioned, and in order to be conservative a conversion of 75 per cent will be used in this estimate, this giving 104 tons of absolute acid, or say 196 tons of 53 %, or 36° Bé. nitric acid per month.

Owing to the rapid fluctuation of the prices of all the materials entering into a construction of this character at the present time, an estimate covering the cost of a plant for producing 196 tons of acid per month can only be indicative, and it is given as such in this statement.

Assuming that one catalyzer can convert 500 pounds of ammonia per day, a plant for the above purpose would require eight catalyzers, five of which would be in constant use, and three in reserve, each catalyzer requiring 4067 grains of platinum, or $4067 \times 8 = 32{,}536$ grains total.



(Facing Page 158)

Under these conditions, the estimated cost of a plant for the above production would be

Buildings, foundations and supports	$20,000.00
Ammonia apparatus	12,000.00
Catalyzer "	10,000.00
Condensing and absorbing apparatus	25,000.00
Storage tanks	2,000.00
Air compressor and fan	4,000.00
	$73,000.00
Contingencies, 7½ %	5,475.00
	$78,475.00
Platinum contacts, original investment, 32,536 grains, or 2113 grammes at $3.20	$6,761.60
Total cost	$85,236.60

OPERATING EXPENSE

1. *Ammonia.* The raw ammonia liquor, containing 75,000 pounds of NH_3 per month, can probably be purchased at 6 cents per pound of NH_3, or $4500.00 per month.

2. *Steam.* With a 1 per cent ammonia liquor, there will be required $75,000 \times 23.53 = 1,764,750$ pounds of steam per month, which at 20 cents per M., will cost $352.95.

3. *Lime.* Allow 0.8 pound of lime per pound of ammonia or $75,000 \times 0.8 = 60,000$ pounds, or 30 tons per month, which, at $8.50 per ton, will cost $255.00.

4. *Cooling Water.* Allow 55,000 gallons per day, or 1,650,000 gallons per month, equivalent to 220,000 cubic feet at 65 cents per M., or $143.00 per month.

5. *Power.* A plant of this size will require about 25 HP. for its operation, or say 13,500 K.W.H. per month, which, at 2 cents per K.W.H., will cost $270.00.

6. *Current for Catalyzer.* The plant will produce 104 tons of absolute HNO_3 per month, and as each 100 pounds requires 4.9 K.W.H. to maintain the temperature in the catalyzer, or say 5 K.W.H., the current per month will be 10,400 K.W.H. at 2 cents, or $208.00.

7. *Platinum.* If the platinum contact is to be renewed each month, each contact weighing 4067 grains, or say 264 grammes, five of these, or 1320 grammes, will have to be renewed monthly, and allowing 10 cents

per gramme for the difference between scrap and new platinum, the replace platinum per month will cost $132.00.

8. *Wages.* Two men will be required per shift to operate valves and cocks, and one additional helper per day, or

6 men at $2.50 = $15.00
1 man at 2.00 = 2.00

$17.00 per day,

or $510.00 per month, to which should be added $125.00 for superintendance, making a total of $635.00 per month.

9. *Repairs.* The repairs on a plant of this size are estimated at about $175.00 per month.

Summary of Cost of Manufacture.

1. Ammonia	$4500.00
2. Steam	352.95
3. Lime	255.00
4. Water	143.00
5. Power	270.00
6. Electric current	208.00
7. Platinum	132.00
8. Wages	635.00
9. Repairs	175.00
12% for interest and depreciation on $78,475.00, per month	784.75
Total cost per month	$7455.70

or say 2.30 cents per pound of 36° Bé. acid.

Production — 324,000 lbs. of 36° Bé. HNO_3 @ 6¢	$19,440.00
Cost of manufacture	7,455.70
Estimated profit per month	11,984.30

The above values are of course only comparative, as the costs of raw material, the efficiency of the plant, and the selling value of the nitric acid are dependent upon local conditions and market for the product.

If ammonuim nitrate, instead of nitric acid, is to be the end product, the nitric acid as produced above must be neutralized with an additional quantity of ammonia, this neutralization being conducted in wooden vats, the resultant liquor being then evaporated so as to cause the salts to crystallize out. The salts are dried in hydro-extractors, and are ready for sale, while the small amount remaining in the mother liquor is also dried and disposed of as a second grade product.

An installation for the production of ammonium nitrate, besides the apparatus specified above, requires in addition another ammonia purifying plant, vacuum evaporators, hydro-extractors, and other appurtenances, it being estimated that this additional plant including buildings will cost approximately $45,000.00.

This will also require 63,000 additional pounds of NH_3 for neutralization, and the total ammonia used will produce 270,000 pounds, or 135 tons of ammonium nitrate.

Cost of Manufacture.

Cost as given for nitric acid	$7,455.70
63,000 lbs. NH_3 @ 6¢	3,780.00
Additional labor @ $25.00 per day	750.00
Purifying additional NH_3, evaporating and drying the salt	1890.00
12% for interest and depreciation on $45,000.00, per month	450.00
Total cost per month	$14,325.70

or say 5.30 cents per pound.

Production — 270,000 pounds ammonium nitrate at 15¢	$40,500.00
Cost of Manufacture	14,325.70
Estimated profit per month	$26,174.30

The profits here indicated are of course very high, but war conditions have greatly increased the value of both nitric acid and ammonium nitrate beyond normal figures; these prices cannot continue, but as the installation can be quickly amortized at present, the plant should be paid for when normal conditions return, and a normal manufacturer's profit may then be expected.

In neither of the cases cited above has a boiler plant been included, as it is presumed that the works contemplating such an installation would have the steam to spare from its present output.

Nitric Acid from Coal Gas. The Häusser process for the production of nitric acid from coal gas lends itself excellently to such coke-oven plants as have an excess of gas, or in such localities where nitric acid may have more commercial value than would ammonium sulphate, and consists of converting the nitrogen in the gas into nitric acid by explosion. A large scale trial plant operating under this process was built at the Nuremberg Gas Works, Germany, before the war, but it is understood that this plant has been considerably modified since then.

The explosion of the gas is effected in steel explosion-proof vessels, these vessels being surrounded by a water-jacket, and to which the air and gas were admitted under pressure through separate valves in the original plant. Ignition of the charge was accomplished by means of a high-tension electric spark derived from a magneto attached to one side of the vessel, this magneto being connected with, and driven from, the same mechanism which operates the air and gas valves.

The chemical reactions involved in this process are of an exceedingly simple nature, the nitrogen combines with the oxygen to form nitric oxide, or

$$N_2 + O_2 = 2NO,$$

and these nitric-oxide mixtures are cooled and passed into a gas holder, where sufficient time of storage is allowed for oxidation to take place, or

$$2NO + O_2 = 2NO_2.$$

The nitrogen peroxide thus formed by oxidation is conducted to counter-absorption vessels where, due to reaction with water, it forms a mixture of nitric and nitrous acid, or

$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

The nitrous acid thus formed is then oxidized to nitric acid by means of an excess of oxygen. The acid obtained in this manner varies in strength from between 30 and 50 per cent, and the weak product is usually evaporated and re-distilled in order to produce a concentrated solution. The waste gases from the plant contain some nitric oxide, and they are therefore treated in special washing towers, thus recovering the greatest possible quantity of nitrous products. It is estimated that between 2 and 3 per cent of the original nitric oxide gas is discharged with the waste products.

It is understood that the original plant built at Nuremberg has been considerably modified, this modification relating particularly to the explosion chamber, these changes having increased the efficiency of the process beyond expectations.

The later design of plant embraces a battery of chambers, or bombs, the entire battery being connected to two compressors, and instead of the gas and air being compressed together, as in the old plant, they are now dealt with separately. High

temperature is essential during explosion, and therefore the air, after compression, is passed through a specially designed pre-heater operated by gas; owing to temperature conditions, it is also essential that a small proportion of pure oxygen be regularly mixed with the air in the compressor.

The latest form of container is driven through gearing from an electric motor, and it is supplied with four valves, the speed of the motor determining the number of explosions per minute. It is also essential that the waste products be cooled rapidly, as otherwise there would be a tendency for the nitric acid to undergo decomposition, and a special exhaust-valve is therefore provided for the purpose of facilitating a drop in temperature.

A condenser coil, immersed in water, is located immediately after the outlet from the bomb, or explosion chamber, the water resulting from the explosion being thrown down in this coil and then drawn off. Practice requires that the explosions be so regulated that they occur in each bomb at the rate of about sixty per minute, and it is stated that, within limits, the greater the capacity of the explosion chamber the larger will be the yield per unit of gas.

This process can be applied to producer gas as well as to all low-grade gas, and as a general statement it may be said that the yield in nitric acid, employing coke-oven gas, will be about $6\frac{1}{4}$ pounds of acid per 1000 cubic feet of gas exploded, but this is probably a maximum condition.

CHAPTER V

BENZOL

While the removal of benzol from gas is not of remunerative interest to the coal-gas producer under the present antiquated standard of gas sale by candle-power, it is of special interest to the by-product coke-oven operator, and as all of the preceding data applies to both of these producers, the method of removing and purifying benzol is herewith included.

Benzol and its homologues were first used as dissolving, purifying and cleaning agents, and for many years their most important function lay in the production of aniline dyes by conversion into $C_6H_5NO_2$ and then into $C_6H_5NH_2$, thus forming a raw basic material which is used in the preparation of artificial organic paints and dyes.

Benzol also forms the basis for the production of artificial perfumes and in the preparation of pharmaceutic compounds, as well as in the production of saccharine, a substitute for sugar.

A very important industrial purpose is served by benzol and its homologues in the production of explosives, such as nitro-benzol and trinitro-toluol.

Benzol is also used for carburetting illuminating gas, an important function where straight coal gas is sold on the candle-power basis; but its most modern as well as important use is its substitution for gasoline as motor fuel, and it is claimed that if benzol is mixed with toluol all carbonizing and sooting of cylinders and sparkers is avoided; this mixed fuel also being non-freezing under ordinary conditions.

All of these uses have created a constant demand for benzol, and the market price is such that its removal from the gas is a very profitable undertaking.

F. Puening, of the Koppers Company, states that the average American coal will produce about two gallons of

benzol per ton carbonized, and if it is compared with gasoline as motor fuel the producer should receive 15 cents per gallon, while the cost of production in a fair sized plant should not exceed 6 cents per gallon; Puening also states that if the benzol in the 14,800,000 tons of coal coked in the 6200 by-product coke ovens in the United States per year is extracted, 29,600,000 gallons having a value of $4,400,000 would be produced, thus making benzol recovery a conservation of resources which would add greatly in reducing the cost of a ton of coke.

Benzol is one of the hydro-carbon compounds which escapes with the gas produced during the dry distillation of coal, and owing to the fact that it is a low volatile it is retained in the gas at temperatures as low as 60° F., the other hydro-carbons being higher volatiles and therefore condensing at the various intermediate temperatures above 60°; the condensation of the other high volatile oils, however, dissolves and absorbs about 5 per cent of the total benzol contained in the gas.

Toluol, xylol, and some other high boiling compounds, such as solvent naphtha, are known as homologues of benzol, and these are found in the volatile portion of the coal and consequently in the resultant gas.

Benzol, C_6H_6, is a colorless fluid and it greatly resembles gasoline; its specific gravity is 0.88, its boiling point 191° F., and its flash point 17.6° F., solidifying at 32° F. into large rombic crystals which melt at 37.5° F.

Toluol, $C_6H_5CH_3$, so closely approaches the appearance of benzol that it is difficult to distinguish one from the other by ordinary means; its specific gravity is 0.87, boiling point 230°, and freezing point −130° F.

Xylol, $C_6H_4(CH_3)_2$, is a combination of three products, closely resembling benzol and toluol and having a specific gravity of 87, the three boiling points being at 278.6° F., 282.2° F., and 7.6° F.

Solvent naphtha is a compound made up of several hydrocarbons, but their exact combination is only partially known. The name "solvent naphtha" is due to its very high solvent effect on rubber. It has a specific gravity of 0.87, and a boiling point of from 302° F. to 356° F.

These characteristics of benzol and its homologues only hold true for these products in chemically pure form, and considerable differences are found in the products as received from coal gas or tar, due to the fact that as such by-products they exist as more or less of a mixture, and repeated distillations are necessary to even approach the pure article, but as far as the by-product producer is concerned, the methods of recovery and purification to be explained later will produce the usual commercial product, the rectification for purity being left to the chemical manufacturer.

Germany is the largest producer of benzol, and there are but few coke-oven plants without their benzol recovery system; therefore, if it has been found to be so remunerative in Germany to recover this by-product the example should be followed in the United States, where some coke-ovens are still operated without efficient by-product recovery.

Puening states in the "Gas Record" that the profits accruing from benzol plants in Europe are very high, having ranged from 50 to 100 per cent upon the investment during the last few years. He also states that, due to several circumstances, the profits in the United States have not been so large, but as seen from the following tabulation these expected profits are sufficient to make the investment give very handsome returns. He bases his calculation on a plant carbonizing 2000 net tons of dry coal per day, with the recovery of two gallons of benzol and its homologues per net ton of coal, or

YEARLY RECOVERY

Benzol, 67 per cent	978,000	gallons
Toluol, 16 per cent	234,000	"
Xylol, 8 per cent	117,000	"
Solvent naphtha, 9 per cent	131,000	"
Total	1,460,000	gallons

With a gross income of:

1,460,000 gallons at 15 cents	$219,000.00
Crude naphthalene, 330 net tons at $5.00	1,650.00
Regenerated acid of 40° Bé., 360 net tons at $6.00	2,160.00
Total gross income	$222,810.00

The operating expense per year being:

Raw material, consisting of wash oil, sulphuric acid, caustic soda	$15,000.00
Steam for distillation, air compressor, loading pumps, acid regeneration and cooling water	15,000.00
Electric power for water pumps, oil pumps, agitator, illumination.	6,200.00
Wages for three distillers and two helpers	5,000.00
Overhead expenses, fire insurance, maintenance and depreciation, assuming the cost of the complete plant to be about $300,000.00,	$30,000.00
Calorific loss of the gas	13,000.00
Total operating expense	$84,200.00

giving a net profit of $222,810.00 − $84,200.00 = $138,610.00 or 46 per cent on the investment capital, and making the cost of producing one gallon

$$\frac{\$84,200.00}{1,460,000} = 5.8 \text{ cents.}$$

This profit is of course dependent upon the selling price of benzol and the cost of raw material, but as it seems to be an established fact that benzol will soon be an active competitor of gasoline for motor fuel, the selling market will probably be governed by the price paid for gasoline; the latter price is increasing daily, and benzol should be subject to the same conditions. The prices paid for benzol from 1881 to 1913 are shown in Diagram IV.

The first commercial benzol plant was built by F. Brunck in Germany in 1887, and since then the development of this system has been very rapid; in spite of the fact that several builders are engaged in erecting benzol recovery plants, the system as laid down by Brunck still maintains, the differences lying only in details, therefore a complete description of operation covering any one system will practically hold good for all others.

THE KOPPERS SYSTEM OF BENZOL RECOVERY AND PURIFICATION[1]

Benzol is recovered from coal gas after the tar and ammonia have been removed; in plants where the ammonia is removed from the gas by the water absorption process the gas usually has a temperature of from 68° to 100° F., while where the direct sulphatation in acid baths is practised the

[1] F. Puening in "Gas Record."

gas temperature is usually from 108° to 170° F., but, as the treatment for benzol should be carried out at about 77° F., the gas must be cooled before entering the benzol scrubbers if its temperature exceeds this figure. After the gas has been cooled to the required temperature it is admitted into the benzol washers (*A*) (Fig. 36), where it is brought into

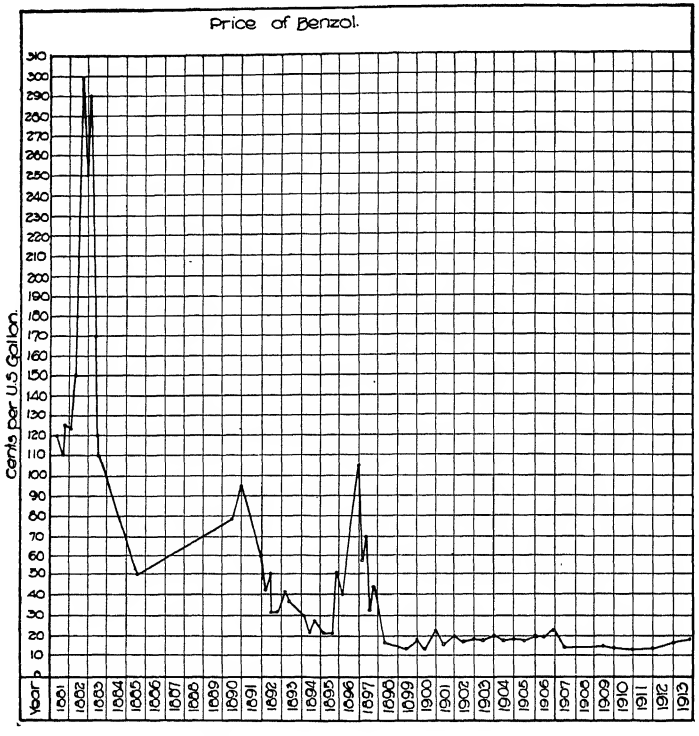


Diagram IV. — Prices of Benzol.

intimate contact with wash oils which at low temperatures are capable of dissolving the benzol constituents and which, after being heated to about 266° F., will again release these constituents.

The principal oil used in Europe for this purpose consists of tar oil of which not more than 5 per cent will distil below 390° F., 90 per cent will distil between 390° and 572° F.; and the naphthalene content must not exceed 7 per

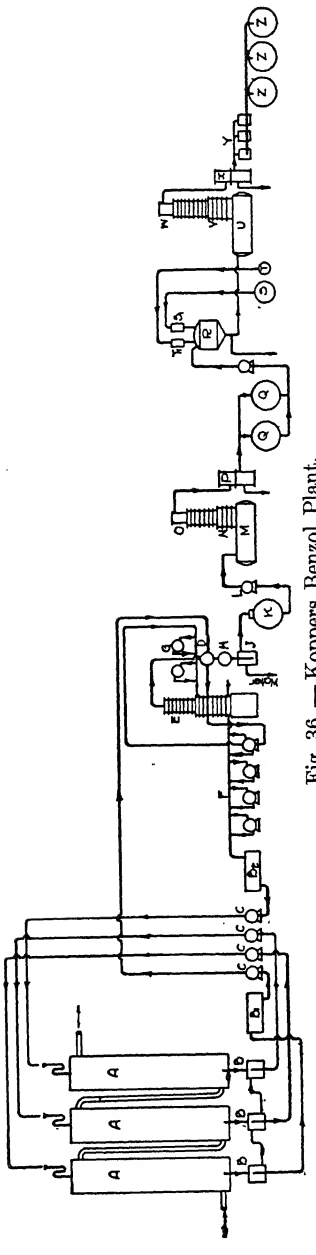


Fig. 36. — Koppers Benzol Plant.

cent, while the water content shall not be more than 1 per cent, and the oil shall contain only traces of anthracene.

This wash oil is taken from the tanks (B) and (B_2) by the pumps (C), and is pumped successively over the benzol washer (A), the current of the wash oil being counter to that of the gas. The wash oil is spread out over the hurdles or trays contained in the towers (A), and it absorbs the benzol constituents up to within very small quantities, finally being delivered to the tank (B_1) in a saturated state. From tank (B_1) the saturated wash oil is delivered to the benzol recovery plant, where it is heated for the purpose of driving off the absorbed benzol constituents.

In order to use as small an amount of steam as possible for heating the enriched wash oil, Koppers causes all of the heat used to distil the wash oil to be transferred to the cold enriched oil on its passage to the still. This cold wash oil enters the heat exchanger (D), where it is heated to about 175° F. by benzol and steam vapors issuing from the still (E). This oil now passes through a second heat exchanger in which it is preheated to a temperature of about 212° F. by means of the hot debenzolized wash oil issuing from the still (E). It is then heated to about

266° F. by means of live steam in one of the superheaters (*G*) for the purpose of driving off the water contained in it and thus rendering it possible to separate the naphthalene.

This water is transferred to the oil from the wet gases, the latter having been cooled to below their point of saturation; again, it may happen that the oils are found to be cooler than the saturated gas, in which case water is precipitated. The naphthalene is washed from the gas in a manner similar to that of washing out benzol and its homologues. Puening states that 1000 cubic feet of gas contains 0.05 pound of naphthalene at a temperature of 80° F., and it therefore becomes necessary to liberate the naphthalene absorbed by the wash oil, as its presence increases the viscosity and decreases the absorbing power of the oil.

At a temperature of 266° F. in the superheater (*G*), all benzol, toluol, and water is expelled, and the oil with its burden of xylol, solvent naphtha and naphthalene now enters the still (*E*). The oil flows through the lower portion of this apparatus and also through its individual chambers, the steam being blown directly into the lowest part of the still, thence traveling in a direction counter to that of the oil, thus driving off all xylol, solvent-naphtha, and naphthalene from the wash oil. The resultant mixture of benzol and water vapors passes through the upper portion of the still, where crude rectification is performed and where all liquid entrained wash oil particles are separated from the vapors. The benzol and water vapors issuing from the superheater (*G*) enter the upper portion of the still where they are rectified in conjunction with the other vapors.

These vapors now issue from the top of the still at a temperature of about 220° F. and enter the heat exchanger (*D*), where they are nearly all condensed and, as stated before, the enriched wash oil is preheated by this exchange of heat. The remaining vapors and the condensates formed in the heat exchanger now enter the water cooler (*H*), where the vapors are completely condensed and all condensates are cooled down to about atmospheric temperature. These condensates, water and light oils, enter the separator (*J*), where they are separated due to their difference in specific gravity.

This so-called light oil is a mixture of crude and impure benzol, toluol, xylol, solvent naphtha, naphthalene, and a portion of the wash oil, and it is collected in the collecting tank (*K*), where it is stored for further fractionation and purification, while the water from the separator is led to the waste liquor tank, or, if it contains any ammonia, it may be sent to the ammonia plant. The wash oil, which has thus been freed of benzol and naphthalene, leaves the still at a temperature of about 257° F. and enters the heat exchanger, where it transfers a portion of its heat to the enriched wash oil, after which it enters the oil coolers (*F*), where it is cooled by water to a temperature of about 77° F., being then delivered to the wash oil tank (B_2), from whence it is again pumped into the scrubbers.

The light oil is now transferred from the storage tank (*K*) to the still tank (*M*), where it is fractionated into its components, the still tank having a capacity of from 6000 to 12,000 gallons, as this larger capacity permits of more decided fractionations than would a smaller one. The oil is heated here by means of two internal-heating coils and one steam spray; due to this heat, the distillation of the light oil begins at a temperature of about 176° F., at which point benzol is driven off, the vapors passing through the rectifying column (*N*) and then through the dephlegmator (*O*). The construction of this rectifying column is similar to that of the usual ammonia or spirit still. The dephlegmator is a water-cooled tubular cooler arranged to cool the vapor mixture, the heavier portions condensing and draining back through the rectifying column, while the fresh rising vapors evaporate the lighter portions of this condensate.

From the dephlegmator the vapors thus rectified pass into the cooler (*P*), which is provided with vertical water-cooled tubes in the upper section, where the vapors condense and the resultant condensate is cooled to about atmospheric temperature. The lower portion of this cooler acts as a separator, separating the benzols from water in those cases where direct steam is used for distillation. The various benzol products then drain from the cooler and separator (*P*) into their respective storage tanks (*Q*).

After benzol, toluol, xylol, and solvent naphtha have been

distilled off, any wash oil with its naphthalene burden remains in the still tank (*M*). The products thus secured from 1000 gallons of light oil vary, this variation being not only due to the character of the coal carbonized, but also to the method of operating the light oil plant, but Puening states that the following will represent the average result:

500 gallons of crude benzol,
120 gallons of crude toluol,
60 gallons of crude xylol,
70 gallons of solvent naphtha,

250 gallons of wash oil containing naphthalene remaining in the still tank (*M*).

The boiling points and the amounts of products from this distillation are shown in Diagram V, prepared by Puening;

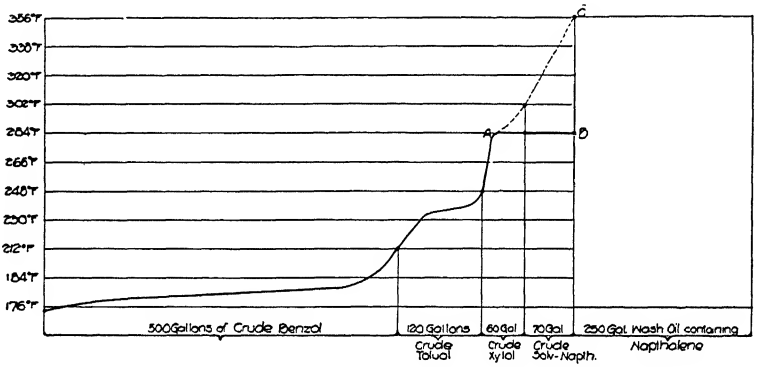


Diagram V.—F. Puening. Boiling Points of, and Products from the Distillation of Light Oil.

it is readily seen that the boiling points differ from those of the pure products, due to the fact that these products are distilled from a mixture of different benzols, the difference being especially noticeable near the points where one kind of benzol should finish and the next one begin.

The temperature up to which indirect steam for distilling can be used is dependent upon the pressure of the live steam available. Generally speaking, it is necessary to use both direct and indirect steam heating for temperatures at and

above 280° F. By referring to Diagram V, it is seen that the distillation of solvent naphtha and a portion of the xylol follows the curve *A–B* at 280° F., while if the temperature is raised above 280° and without the use of indirect steam, distillation will follow the curve *A–C*.

The wash oil retained in the still tank (*M*) is drained into cooling pans, where it is cooled by the atmosphere to crystallize out the naphthalene, after which the oil is drained off and returned to the oil circulating tank (B_2), thus again entering the washing system. A small cooler, for the purpose of cooling the oil to about 175° F., receives the wash oil and naphthalene just before it enters the cooling pans, in order to prevent the giving off of obnoxious odors. The naphthalene thus deposited in the pans may be dried in a centrifugal, thus separating the small amount of oil remaining in the crystals, this naphthalene being sold as a crude product, or it may be mixed with the tar.

The crude benzols in the storage tanks (*Q*) are now further purified by washing them separately in the washer (*R*) with sulphuric acid, caustic soda, and water. This washer consists of a large lead-lined vessel provided with an agitator or centrifugal mixing arrangement; here the benzols are washed with 66° Bé, or 1.84 specific gravity sulphuric acid, the amount used varying for benzol and toluol from 8 to 14 per cent by weight, and for xylol or solvent naphtha from 20 to 24 per cent by weight. The acid is supplied from the storage tank (*S*), it passing through a meter (S_1) before entering the washer. The mixer is located at a height which permits of discharging the acid in the bottom of the washer, near the level of the benzol, and to distribute it in such manner as to obtain a thorough mixture. This mixing or washing is performed in about thirty minutes, after which the agitator is shut down and twenty minutes allowed for the used acid to settle to the bottom of the washer, the acid being used to separate the unsaturated hydro-carbons, principally phenols and olefines. The majority of these impurities in conjunction with the acid form thick resinous compounds, which are insoluble in benzol and which, due to their high specific gravity, settle out in the bottom of the washer, but a small portion of these resinous bodies, es-

pecially the polymeric olefines, dissolve in the benzol and thus give it a brown color; redistillation will separate these dissolved olefines from the benzol and thereby cause the brown color to disappear, the acid used being later regenerated.

The benzol is now washed with water in order to remove the remaining acid, after which a 16° Bé. caustic soda solution is run into the washer for the purpose of neutralizing any remaining traces of the acid in the benzol, this latter solution being prepared in tank (T), and the proper quantity required measured in tank (T_1) before admittance into the washer. After being properly mixed with the benzol, the caustic soda is permitted to settle, and is then drained off, the benzol being again washed with water in order to remove any traces of caustic soda. The acid usually reduces the volume of the benzol, due to the extraction of impurities, this reduction amounting to from 5 to 7 per cent of benzol and toluol, and it may be as high as 20 to 30 per cent of xylol and solvent naphtha.

The benzol from the washer (R) is now delivered to the still tank (U), this latter vessel being of similar construction to tank (M), but it is advisable to interpose storage tanks for washed benzol between the washer (R) and the still tank (U) in order to permit the washer to operate independently of the still. The still tank (U) is provided with heating coils, an especially high rectifying column (V), and a dephlegmator (W). After passing through the rectifier and dephlegmator, the vapors pass into the cooler (X), where they are condensed and cooled to about atmospheric temperature; the condensates from the cooler drain into the receivers (Y), where the quality of the product is tested before being admitted into the storage tanks (Z).

This latter distillation is dependent upon the character of the final product desired. Puening states that distillation carried out as described above improves the limits of the boiling points and that the finished product more closely approaches the chemical characteristics of the pure benzols. However, due to the fact that the largest demand for benzol in the present market will probably require products of rather inexact boiling points, the last distillation will only have to separate the benzol from the resinous olefines held

in suspension, and therefore but little attention need be paid to the final boiling points.

Under these conditions this last distillation will be accomplished very quickly, and the vapors thus produced are sent directly into the cooler (*X*), the rectifier and dephelgmator being by-passed. The benzols produced in this manner are known as "purified benzols," and they will have the same general characteristics as regards their boiling points as have the "crude benzols" shown in Diagram V.

The water and caustic soda used in the washer are drained to the waste sewer, but the acid is conducted to small tanks where it is regenerated to 40° Bé. by mixing it with steam, which condenses while heating the acid, the lighter parts of the resinous compounds being evaporated at the same time; after the steam is shut off and the contents of the tanks cooled, the remaining portions of the resinous compounds solidify, and can then be removed, the 40° Bé. acid being sent to the ammonia plant. These acid boilers must be so arranged as to prevent the emission of any of the resulting vapors, the greater portion of the latter being conducted to condensers, a smaller quantity being usually discharged into the atmosphere.

This last distillation for the production of benzols approaching the pure article in chemical characteristics requires about five times the distilling period required for crude benzol. The still tank (*U*) in the Koppers system is filled with about 10,000 gallons of washed benzol having boiling points as shown in Diagram V, while the distillation is accomplished at the boiling points shown in Diagram VI; in the latter diagram the portion from *A* to *B* shows the forerunnings, which consists of a few per cent of impurities, such as carbon bisulphide, while the portion from *B* to *C* shows "pure benzol," and that from *C* to *D* a mixture of benzol and toluol, the temperature curve of the latter following the line from *C* to *D*.

The amount of "pure benzol" recovered is claimed by Puening to be about 55 per cent of the "crude benzol" run into the washers, and while distilling 10,000 gallons of washed crude toluol, in order to recover "pure toluol," the distillation follows the course of the curve shown in Diagram VII.

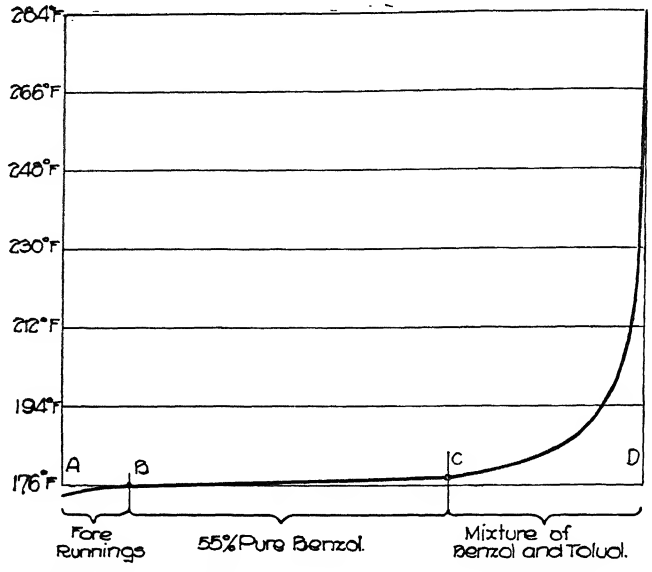


Diagram VI. — Boiling Points and Product — Pure Benzol.

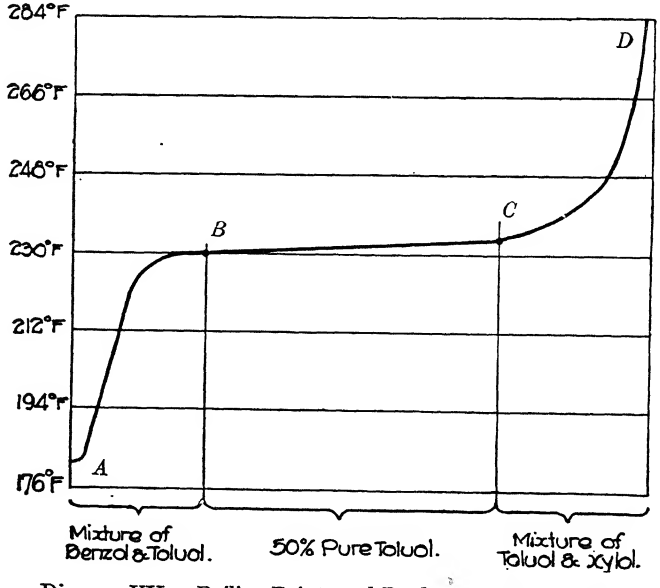


Diagram VII. —Boiling Points and Product — Pure Toluol.

The distillation in this latter instance begins at *A*, a mixture of benzol and toluol being evaporated up to the point *B*, while "pure toluol" results from *B* to *C*. After the toluol has been expelled the distillation follows the curve from *C* to *D*, and produces a mixture of toluol and xylol; the production of "pure xylol" will produce a curve similar to the one shown in Diagram VII. Diagrams VI and VII for "pure benzol" and for "pure toluol" both show a slight increase in temperature, amounting to 1.1° F. for benzol, and to 1.8° F. for toluol between the points *B* and *C*, an indication that although these products are termed "pure," they are not absolutely chemically so, since if they were, the curve would not rise at all. Usually the mixtures produced between *A* and *B*, and *C* and *D* in Diagrams VI and VII, are mixed and sold as such. Table XVIIIA shows the benzol specification as prepared by the "Deutsche Benzol Vereinigung," which company controls the benzol trade of Germany; column 4 of this table relates to the chemical purity of the product.

The Feld System:

In the Feld system (Fig. 37) the gas is washed in the washers (*A*) with light oil in a manner similar to that of Koppers, the saturated oil entering the receivers (1) and (2), finally flowing from (1) to the wash oil tank (4), the fresh oil to the washers being pumped from tank (5). From the wash oil tank (4) the saturated oil is pumped into the regulator (*B*), flowing from thence into the outflow heater (*C*), rising up through the still preheater (*D*) and steam preheater (*E*), and finally entering the column still (*F*), where it is distilled by means of both direct and indirect steam. The wash oil flows from the bottom of the still and enters the outflow preheater (*C*), where it serves to heat the wash oil coming from the regulator (*B*), after which it flows through the final cooler (*G*), where it is cooled by means of cold water, then entering fresh oil tank (5), from whence it is sent back into the washing system.

Light oil vapors mixed with water vapors leave the column still (*F*) and pass through the still preheater (*D*), where they serve to impart additional heat to the saturated wash oil on the way to the still, the vapors being thus condensed

TABLE XVIIIA. — SPECIFICATION OF THE DEUTSCHE BENZOL VEREINIGUNG

Description	Boiling points F.	Color	Reactions of sulphuric acid	Remarks Specific gravity 60° F.
90 % crude benzol	90 to 93 % up to 212°	....	....	Specific gravity 0.86 – 0.88
90 % benzol purified ...	90 to 93 % up to 212°	Water color	1.5	Specific gravity about 0.88
50 % benzol purified ...	50 % to 212°, 90 % to 248°....	Water color	1.5	Specific gravity about 0.88
Pure benzol	90 % inside of 1.1°.....	Water color	0.3	Specific gravity about 0.88
	95 % inside of 1.8°			No specification for solidifying point
Crude toluol.....	90 % between 212° and 248° ..	Water color		
Purified toluol	90 % between 212° and 248° ..	Water color	Light yellow	Specific gravity about 0.87
Pure toluol	90 % inside of 1.8°.....	Water color	0.3	Specific gravity about 0.87
	95 % inside of 2.4°.....			
Crude xylol	90 % between 248° and 302° ..	Water color to yellow.	Light yellow	Specific gravity 0.87
Purified xylol	90 % between 248° and 293° ..	Water color		Light proof
Pure xylol.....	90 % inside of 6.5°.....		2.0	Specific gravity 0.86
	95 % inside of 8.1°.....	Water color		
Crude solvent naphtha	The distillation should not	Water color to light ..	Light yellow	Specific gravity 0.87
Solvent naphtha-I-purified.....	start below 248° at least 90 % must distil over up to 320°	Yellow.....		Light proof, mild aroma
Solvent naphtha-II-purified	90 % between 275° and 356° ..	Water color to yellow.	Precipitation of brown yellow reddish masses allowed	Specific gravity 0.89 Not quite light proof

in (*D*); this condensate enters the separator (*H*), where the the water is separated from the oils, the water being led away while the light oils flow into the oil receiver (*J*), the latter being provided with a water pocket in the bottom for the purpose of collecting any entrained water.

At stated intervals the still receiver (*K*) is charged with light oils from tank (*J*), where they are fractionately separated through distillation by means of direct and indirect steam. The vapors from the still pass through the rectifier (*L*), where the vapors of high boiling points, such as toluol and xylol, are condensed, and the partially purified benzol enters the dephlegmator (*M*). The temperature of the cooling water in the dephlegmator is kept at about 80° C.; the benzol vapors pass through the pipe system of the dephlegmator without condensation, being later cooled and condensed by means of cold water in the final cooler (*N*), passing from thence into the separator (*O*), and then into the receiver (*P*), one of the latter being provided for each of the distillates, as after the benzol has been removed the toluol, xylol and solvent naphtha are driven off.

After distillation has been completed, the wash oils remaining in the still tank (*K*) are run into the cooling pans (3), where the naphthalene crystallizes out.

The raw benzol is now led to the purifier (*S*), where it is treated with sulphuric acid, caustic soda, and water as in the Koppers system, after which it is again distilled in still (*U*) and rectified, dephlegmated, and separated, the final products being found in tanks (*Z*).

In the extraction of benzol direct contact water coolers should be used for cooling the gas; usually they consist of tall, cylindrical shells filled with wooden trays, the gas entering at the bottom and flowing in a direction counter to that of the cooling water, which latter enters at the top.

Puening states that when tubular coolers were formerly used, the gas being separated from the water through the walls of the tubes, it was impossible to cool the gas to a temperature as low as that in direct contact cooling, the lower temperature being required for efficient benzol extraction, as its absorption is best at low temperatures; besides this, the naphthalene deposits prevented the cooling

of the gas by checking the transfer of heat through the tubes, while in the direct contact coolers the separated naphthalene is washed out by the water passing through the cooler, and thus occasional deposits will not affect the extraction efficiency.

The naphthalene carried by the water flowing from the coolers is easily separated out by crystallization. Instead of contact coolers such as described above, Feld uses his vertical centrifugal washers for cooling the gas by direct contact with water.

Puening also states that hurdle washers are used to a great extent in Germany and England for benzol absorption, the hurdles in these towers being so arranged as to cause the gas to take a zigzag direction in passing through, the hurdles consisting of wooden planks about $1\frac{3}{16}$" wide spaced $\frac{11}{16}$" apart, their lower edges being serrated to assist the dripping oil to distribute itself over the next lower lying layer.

Hirzel uses three different kinds of washers, the first one being known as a tuyre washer and consisting of a steel shell provided with from 200 to 400 spray nozzles so arranged as to fill the entire space on the inside with a fine spray of oil; the second washer is built in sections, similar to an ammonia still, the bottom of each section being provided with numerous tubes covered with seal caps, the latter dipping into the oil in each section, thus causing the gas, which enters the bottom of the washer, to pass up and break the seal at each hood, being thus mixed with the wash oil; the third washer is of the hurdle type as explained above.

Feld uses his vertical centrifugal washer for benzol extraction, and it has been found exceedingly efficient on this duty, throwing far less back pressure than any of the other devices used for this purpose.

Koppers advises that steel be used in the construction of oil heating, distilling and cooling devices, except in the column rectifier, where cast iron is more suitable; steel is a suitable material where the temperatures do not exceed 210° F., but at this temperature and above cast iron should be used on account of the corrosive effect of the hot oils containing possible slight traces of ammonia.

Oil superheaters are subjected to the most severe corrosive conditions, and spare heaters should be provided, so arranged that they can easily be shunted into or out of the system. Koppers recommends that oil superheaters with spiral tubes be used only in small plants, because repairs are generally very high in cost due to entirely replacing the coils. Koppers also arranges his apparatus for heating and cooling the wash oil in such manner that each individual unit can easily be taken out without disturbing the other apparatus.

As the cast iron stills do not corrode, it is not necessary to provide spare stills, and Koppers states that stills have been in operation for from 10 to 15 years without repairs. The construction of oil heaters and coolers requires special attention, because hot oils and benzol escape through the smallest opening produced by expansion and contraction during changes in temperature.

Hirzel does not agree with the other designers as regards the method of distilling the oil and driving off the benzol vapors, and has made his views in this particular a subject of U. S. patent No. 991,205, issued May 2, 1911.

He states that the ordinary methods of fractional distillation, or the separation of the components of a mixed liquid, are usually based on the differences existing in the boiling points of the components and, as explained above, the usual method consists of a series of regulated and methodical boilings at different temperatures, thus boiling away the component of a lower boiling point from the one of a higher boiling point in a column still. Hirzel states that the balancing effect between the base heating and the cooling due to the skin contact of the shell in the usual still, as well as the introduction of a relatively cool liquid at the top, causes a regular diminution of heat upward, and by introducing a mixed liquid at the top of the column and causing it to travel successively through the liquid holding devices of the still, it is boiled at a series of successively increasing temperatures; thus the vapors due to the boiling liquid in each liquid holding device, or tray of the still, serve to boil the liquid in the device next above, condensing therein the greater portion of their high-boiling components, and adding the vapor of their low-boiling components to that which is there evolved.

Hirzel claims that this method, which is suitable for some purposes, is not well adapted for boiling oils containing many constituents.

As explained before, the boiling point of a mixture of mutually soluble liquids is perfectly definite with a given mixture under given conditions, and depends not only upon the respective boiling points of its constituents and their relative proportions, but also upon many other factors, such as vapor tensions at different temperatures, mutual affinity and solubility in liquid and vapor states, pressure, etc.

Hirzel states that when these conditions change, these factors also change quite independently of each other, and that with complex mixtures there is no simple relation between the compositions of the vapors evolved in boiling at different temperatures; or, in other words, there is no certainty as to the result which will be obtained in running such a mixture through the usual column still.

The subject of the above patent calls for simplified conditions of distillation, and Hirzel claims that the results are correspondingly improved by departing from the usual practice of relying solely upon differences in boiling points, but rather depending upon differences in vapor tensions.

The liquid to be treated is converted into a large area film, and, by a suitable arrangement of heating elements, the film thus formed is uniformly heated to a temperature approaching, but below the boiling point of the constituent to be removed, or near its point of maximum tension. This film is treated with a heated current of gas or vapor into which the constituent in question volatilizes and from which it may be later removed by condensation, or in other words, the operation consists of evaporation instead of the boiling of ordinary fractional distillation methods, the still being so arranged as to practically maintain a uniform temperature throughout the entire height.

Hirzel's scheme is shown in Fig. 38, where the washers are represented as (A), two or more being required, dependent upon conditions, with the usual gas connections, the wash oil being supplied to the first washer from tank (B) by means of pump (C_1), the wash oil flowing from the bottom of the washer into tank (D), and being forwarded from there by

pump (C_2) to the top of the second washer (A_1), flowing from thence into the saturated oil tank (E).

The saturated oil flows from (E) into the heat interchanger (F), where it is heated by the vapors coming from the still (G), and then flowing into the top of the still. In the still

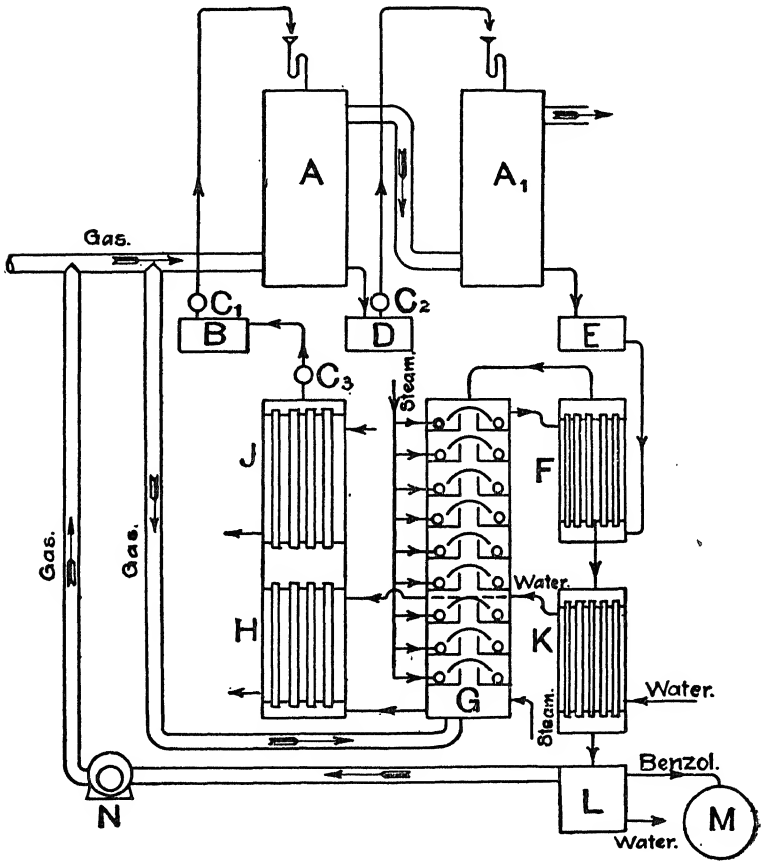


Fig. 38. — Hirzel Benzol Plant.

the heated oil is deprived of its volatile constituents, or crude benzol, the oil leaving the base of the still and flowing into the cooler (H), and chiller (J), both being devices of the tubular condenser type, the cooler being provided with an inlet and an outlet for cooling water, while the chiller is supplied with similar connections for carrying a chilling fluid.

The wash oil is now ready for absorption purposes in the washer again, and it is therefore pumped away from the chiller by pump (C_3) and sent to the wash oil tank (B).

The Hirzel still is of peculiar construction, as it is not intended that it shall be subjected to a differential heat from the bottom to the top, as is usual in the ordinary column still, but it is uniformly heated throughout, because Hirzel does not wish to fractionate the liquid treated, as is usually done by a series of successive boilings, but only to remove a single desired constituent by exposing the liquid in a large film area uniformly heated throughout to the proper temperature.

The still is provided with a series of annular trays, each tray being supplied with a steam coil, all coils communicating with a header on the outside of the still. As Hirzel does not desire either skin cooling or differential heating, he lags the entire still with insulating material to assist in maintaining a uniform temperature. Each annular tray is supplied with a hood over the central aperture, a current of heated indifferent gas being sent upward through these apertures against the descending filmed liquid to strip the liquid of its volatile constituents. Hirzel uses either steam for this purpose, or gas from the mains.

The gas (at the temperature at which the benzol still is ordinarily run, about 266° F., steam may be considered a gas) carrying the volatilized benzol leaves the still at the top, passes around the tubes in the heat interchanger (F), thus warming the inflowing wash oil by transferring some of its heat, and then passes down into the condenser (K), where it is cooled by means of water, the water leaving this condenser and entering the wash oil cooler (H). From the condenser (K) the condensed liquids enter the collecting tank (L), and if steam has been used as the carrier, the condensed water accumulates in the bottom of this tank from whence it is drawn off, the condensed benzol flowing out of the top of the tank to the storage vessel (M).

If gas from the mains has been used as the carrier, the gas is removed from the tank (L) by means of the exhauster (N) and returned to the gas system; this gas as it leaves the mains and enters the still is saturated with benzol at the temperature at which it enters, but by being heated in the

still it is capable, according to Hirzel, of absorbing more benzol and thus serves to remove this constituent from the wash oil, depositing this excess in the condenser.

The benzol still used in the Gasser system is a radical departure from all of the others, and consists of a series of long horizontal cells, separated from each other, each cell being supplied with an independent source of heat. It is claimed that this method of construction permits the saturated wash oil to flow to the cells at rather low temperature, and then gradually to heat the various cells to a degree corresponding to the decreased amount of benzol carried by the oil.

The extended form of the cell also makes it possible to force the oil through in a thin film, constantly bringing this film in contact with fresh steam, it being claimed that this procedure is very effective in liberating the benzol. Besides this, the method of constructing this still is such that it can be arranged for any capacity, the additional capacity being secured by adding individual cells.

This same construction is also used for distilling off the partially purified, as well as the purified, benzol, the construction of the cells being such that continuous distillation is claimed, only such an amount of benzol as can be distilled in a given time being admitted into the still.

Figure 38a is a diagram of a light-oil plant for medium sized works, and contemplates the removal of benzol and its homologues from the gas and the driving off of the wash oil from the benzolized oil, returning this wash oil to the system again.

The proper location for a plant of this character is undoubtedly after the purifiers, or especially after the ammonia, has been removed, thus avoiding an ammonia loss which might occur by the deposition of salts due to the low temperature at which the benzol plant should be operated. If located after the purifiers an added advantage is secured in the removal of corrosion danger due to the action of sulphur compounds. If located ahead of the purifiers, there is a possibility of coating the purifying material with oils which may be entrained and carried over in the gas, thus rendering a portion of the purifiers inactive.

The plant shown in Fig. 38a contemplates the use of a condenser ahead of the benzol washer, in order to reduce the temperature of the gas to as low a point as possible, 70° F. being

a good temperature for effective benzol scrubbing. The benzolized oil from the washer is run into a storage tank, which should be of large proportions in order to separate out any water which may be carried over with the gas, and is pumped from there to an overhead supply tank; the oil from this tank flows into a tubular preheater, where it is heated by the hot debenzolized oil coming from the still, passes thence into a heat-exchanger, where it receives a further increase in temperature from the vapors coming from the still and dephlegmator, and is finally brought to the proper temperature for admission into the still by passing through a superheater, where the temperature is raised by steam.

The debenzolized oil, after passing through the preheater, is cooled in the wash-oil cooler, and passes from there into the wash oil storage tank through a water separator. The light-oil vapors from the still and dephlegmator, after passing through the heat exchanger, pass into the benzol condenser, where they are liquefied, and then through the water separator to the crude benzol storage tank, measuring tanks, not shown on the diagram, being interposed between the water separator and the storage tank.

Great Britain, recognizing the necessity of benzol recovery, due to the present war, has established washing plants in many coal-gas works, both large and small, using creosote or green oil, tar oils, or American gas oil as the washing medium, but no wash oil should be used which will distill under 400° F., this temperature being above the boiling point of benzol and its homologues.

Creosote oil has a specific gravity of 1.04 and contains about 8 per cent of tar acids, distilling between 425° and 540° F., while green oil has a specific gravity of 1.098, distills between 498° and 668° F., and contains no tar acids.

Tar oils distill between 390° and 572° F., but about 5 per cent will distill below 390°; owing to the amount of naphthalene contained in tar oils, they should be carefully selected, as in no case should the oil contain more than 7 per cent of naphthalene.

Gas oil, as a rule, will wash out some of the paraffins from the gas, and it should therefore be subjected to a preliminary distillation in order to remove some of its lighter constituents.

The wash oil used in America is usually a petroleum distillate, known as "straw oil," having a specific gravity of 0.88, or 30° Bé., and of which at least 90 per cent boils between 450° and 630° F.

The average oil used will absorb between 3 and 4 per cent of its own volume or weight in benzol and its homologues, and between 75 and 100 gallons of oil are kept in circulation per ton of coal carbonized, the volume of oil used of course depending upon its absorbing power. A small portion of this oil will have to be replaced from time to time, as some of it will be carried over with the light-oil vapors from the still, but the amount is small.

The principal difficulties encountered in Great Britain, owing to oil washing, have been due to: water in the oil; emulsion of wash oil and water; thickening of oil; naphthalene; lack of fractionation; corrosion, and air locks in the system.

Water in the oil is due to the deposition of water coming from the gas, or it may come from the condensation of steam in the still. Water separators should be applied ahead of the benzol washers, or very large storage tanks should be used to permit of a separation of water from oil by difference in specific gravity. Very wet steam also accounts for this trouble, and superheating the steam will avoid it.

If the wash oil is much cooler than the gas, emulsification may occur, and it is therefore advisable to maintain the temperature of the wash oil a few degrees F. higher than the gas.

Emulsion of wash oil and water may be due to the water coming from the gas being thoroughly mixed with the wash oil in the washers, or, if the benzolized oil is admitted into the still at too low a temperature, condensation may take place.

Thickening of the oil may be due to the evaporation of lighter fractions of the wash oil by steam distillation, this being especially so if the gas is free of tar-fog. If this thickening occurs, it can be remedied by adding a quantity of especially light creosote oil.

Naphthalene troubles may be due to the gas picking up naphthalene from the oil, or to the extraction of the naphthalene carriers from the gas. If due to the first cause, it will be well to look into the naphthalene content of the wash oil, as if the latter does not contain more than 7 per cent, this trouble

should not occur. The use of open steam greatly reduces the quantity of naphthalene in both the gas and the oil, and while its use tends slightly to reduce the quality of the distillate, the best results for both benzol and naphthalene are usually secured when the total distillate consists of half water and half crude benzol.

If the trouble is due to the removal of naphthalene carriers from the gas, it can be corrected by adding solvents to the gas, as explained in Chapter II.

Lack of fractionation was usually found in plants where tar dehydration apparatus, without any modification, was used for debenzolizing the oil. The resultant benzol was found to be of poor quality, and priming of the wash-oil often took place.

Corrosion was found to be quite serious on the parts in contact with hot benzolized oil, providing much ammonia was present, and cast iron was found best adapted to withstand this action.

Trouble with air-locks may be expected by a faulty arrangement of heat exchangers, coolers, etc., in which proper allowance has not been made for the escape of air, this condition requiring that the oil always enter the exchangers at the lowest point and pass out at the highest, otherwise it will be necessary to apply air vents.

Mr. J. W. Shaeffer, of Milwaukee, in his paper read before the American Gas Institute, gives the results of his studies in the loss of heat value due to the removal of the light oils from the gas. He determined the heating value of the light oil to be 17,400 B.T.U. per pound of liquid light oil, and to this he added the latent heat of vaporization of benzol, or 167 B.T.U. per pound, thus making 17,567 B.T.U. the gross heating value of one pound of light-oil vapor; this value is somewhat lower than the corresponding value for pure benzol, the latter being 18,793 B.T.U. Shaeffer accounts for this by the presence of carbon disulphide and other impurities of a lower heat value in the light oil. The latent heat of vaporization was added in order to make the results comparable with calorimeter tests in which the light oil enters the calorimeter in the shape of vapor.

Calorimeter tests were made on the gas before and after oil scrubbing, and the difference in B.T.U. divided by the total

B.T.U. of the gas before benzol scrubbing gave the percentage of actual loss. The B.T.U. per cubic foot of gas after the scrubbers was calculated from

$$\frac{a - 121{,}827b}{1 - 35b}$$

in which a = B.T.U. per cubic foot of gas before scrubbing,
b = gallons of light oil removed per cubic foot of gas,
35 = cubic feet of vapor per gallon of light oil.

The constant 121,827 is the product of 17,567, the B.T.U. per pound of light oil, 7.3 the pounds per gallon of light oil, and 0.95, a correction factor used for correcting the amount of wash oil in the light oil, this amount of wash oil being assumed at 5 per cent.

The average of all calculations showed a theoretical loss of 4.45 per cent, while the actual loss as determined by calorimeter tests at the same plants was 4.62 per cent. The above averages are low, because they include plants where the scrubbing resulted in a comparatively low efficiency, and for a plant where the scrubbing is accomplished with a fair degree of efficiency, the loss in heat value will be higher, probably 5.8 per cent. The conclusions reached by Shaeffer were:

1. The actual loss in the gross calorific value of the gas due to the removal of light oil is about 5.8 per cent at plants where the removal takes place with a fair degree of completeness.

2. The theoretical loss is practically the same as the actual loss. This is an average determination.

3. Some plants show a greater actual loss than the theoretical loss and some *vice versa;* all agree within the limits of probable error in determination.

4. The observed loss due to the removal of the light oil is considerably greater than the actual loss. This is accounted for by the difference between the gross and net heating values and an improper air supply to the burners.

5. The observed loss has led many gas engineers to believe that the actual loss is greater than it really is.

6. The true value of light oil in a gas lies in its effectiveness per unit volume. 1.1 per cent of light oil by volume furnished 7.4 per cent of the total heat, which is formed when the gas is burned.

The removal of light oils from the gas therefore involves the burning of more gas to secure a given heating effect, and if 10,500 cubic feet of gas are produced per ton of coal carbonized, the loss of 5.8 per cent in heat value will be equivalent to the loss of 609 cubic feet of gas.

The Public Service Gas Company of New Jersey recently erected a light-oil washing plant at one of its stations, this plant handling about 4,000,000 cubic feet of mixed coal and water gas in 24 hours. Between February 14 and April 1, 1917, this plant treated 183,468,000 cubic feet of gas, of which amount 72,817,000 cubic feet was coal gas and 110,651,000 cubic feet was water gas. The light-oil washing plant removed 87,589 gallons of light oil from this volume of gas, thus averaging 0.477 gallon per 1000 cubic feet of gas washed. After deducting waste and residuals, about 0.35 gallon of benzol products per 1000 cubic feet of gas resulted, this large amount being due to the water gas, which contains more benzol than does coal gas.

The average heating value of the total mixed gas dropped from 620 to 605 B.T.U. and as all the gas made was not washed, this indicated a heating value of about 575 B.T.U. for the washed gas. The illuminating power of the total gas, washed and unwashed, dropped from 20 to 15.88 candles, this indicating a loss of about 7.70 candles of the washed gas.

The quantity of artificial gas used for illuminating purposes, and only a small percentage of this in open-flame burners, is but a small proportion of that used for heating and power operations. The caloric value is the main consideration in the latter case, and this also is true of incandescent mantle lighting, as the lighting effect is not increased with an increase in the candle value of the gas used.

In view of the very small reduction in caloric value resulting from the removal of the benzol homologues, and the future developments in the industrial and chemical fields for these products, the conservation of such products is a telling argument in favor of the replacement of the obsolete candle value standard for gas sales by the more logical calorific standard.

CHAPTER VI

SULPHURIC ACID

Owing to the possible difficulty of securing acid for sulphate manufacture, and the trouble and inconvenience this lack of supply would entail, it may become necessary for the gas-works or coke-oven operator to produce the acid on the plant, and a description of the process of manufacture is therefore given below. Some works may not be large enough to take up acid manufacture individually, but it is possible for several neighboring works to combine, ship their spent oxide, with its sulphur burden, to some central point, and there produce the necessary acid for the benefit of the participants.

Sulphuric acid is made by either the "Contact" process, or the "Chamber" process, either of which is primarily dependent upon the sulphur gases generated by the burning of sulphur-bearing material.

In the "contact" process, the spent oxide, bearing its sulphur burden, is burned in a furnace with air, the sulphur dioxide and other gaseous products of combustion thus produced being later cooled and freed from dust and the greater portion of the moisture content. These purified gases are then mixed with air and passed through a catalyzer, the catalytic agent being either ferric oxide or finely divided platinum. It is absolutely necessary that the impurities be removed from the gas before entering the catalyzer, as otherwise they would act detrimentally on the contact material, and it would soon lose its catalytic power.

The greater portion of the sulphuric acid made, however, is provided by the "chamber" process, the usual product being commercial oil of vitriol, which is not a pure or concentrated article, as it contains only from 60 to 70 per cent of sulphuric acid. The advantage of the "contact" process over the "chamber" process is that in the former a pure, concentrated acid is directly formed, but for purposes of ammonia absorption the "chamber" acid will, as a rule, answer all purposes.

The apparatus required in the "chamber" process embraces the sulphur-burning furnace, combined with a dust separator, or purifier, and niter oven; the Glover tower for cooling the gas, concentrating the chamber acid, and denitrating the nitrous vitriol; the lead reaction chambers; and the Gay-Lussac tower for absorbing the oxides of nitrogen.

In this process, the spent oxide is burned in a furnace, and the gas thus produced in this sulphur furnace contains between 7 and 8 per cent of SO_2, the balance being excess nitrogen and air. The sulphur furnace may be of any type suitable for the purpose, the one shown in the diagram, Fig. 38b, combining the furnace proper, the dust chamber, and the niter oven in one setting. The furnace selected should be of a type which will continuously supply a sulphur gas of constant quality and quantity, and it should produce as little dust as possible; it should be provided with accurate means for regulating the air supply to the burning sulphur, as otherwise some of the sulphur might sublime, and it should also be capable of maintaining a constant temperature at the inlet to the Glover tower. Perhaps the best furnace to meet these requirements is one of the Wedge type, although a large number of furnaces of the general design shown in the diagram are used. The Wedge, or mechanical type of furnace, will give a regular supply of gas, and the composition of the gas will be more constant than that produced in the hand-fired furnace.

The gas leaving the sulphur furnace (B), Fig. 38b, contains dust, and the greater portion of this dust is deposited in the dust chamber (C), under the nitre pots (D), as the gas is caused to take a tortuous path through the chamber. The gases now pass over the niter pots, where the nitric acid required is introduced in the form of a vapor, being generated by the action of sulphuric acid on sodium nitrate. In some plants liquid nitric acid is introduced into the Glover tower, trickling through the filling of the tower together with the nitrous vitriol. The reaction in the niter pots may be expressed as

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4,$$

or the action of sulphuric acid on sodium nitrate, produces nitric acid and sodium acid sulphate, or niter cake.

This mixture of gases is now passed into the Glover tower (F),

through the flue (*E*), an acid-resisting fan, not shown in the diagram, being installed ahead of this tower to give the required draught on the furnace. The gas enters the bottom of the tower and passes up through the packing or filling, the hot gases thus being brought into intimate contact with a down-flowing stream of aqueous sulphuric acid, evaporating the water from this acid, by giving up a portion of its heat, and thus also supplying a portion of the steam or water necessary to produce the required reactions in the lead chambers (*G*), (*H*), and (*J*). This moisture and heat also assist to drive off the lower oxides of nitrogen from the nitrous vitriol fed into the top of the tower, this denitration process being assisted by the simultaneous concentration and action of SO_2, as is shown in the equation

$$2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

The Glover tower is usually erected upon an elevation which will permit the acid to flow from the bottom of the tower through the lead-cooling apparatus and to storage. This tower is usually a lead cylinder about 9 feet in diameter and from 25 to 30 feet high, the lead shell being supported by an external frame of wood, and protected inside for about two-thirds of its height by a lining of acid-resisting bricks. The interior is filled with bricks, or small cylinders of clay to give adequate contact surface to the ascending gases. The upper part of the tower is provided with two lead vessels, one containing nitrous sulphuric acid, about two-thirds of the entire acid used, and the other sulphuric acid from the chambers.

These two acids are distributed by sprays over the entire area of the tower, where they mix and flow down through the filling against the current of hot SO_2 gas coming from the burner. The nitrous vapors are liberated and escape into the top of the tower from where, together with SO_2 and air, they pass out into the first lead chamber. The concentrated sulphuric acid formed here, 60° Bé., collects at the bottom of the tower and passes out to the cooling apparatus and storage.

The reactions in this tower, according to M. Neumann, are of two kinds, that in the lower portion of the tower, where the temperature is at its maximum, being a reducing action, and in the upper portion, where the temperature is at a minimum, an oxidizing action.

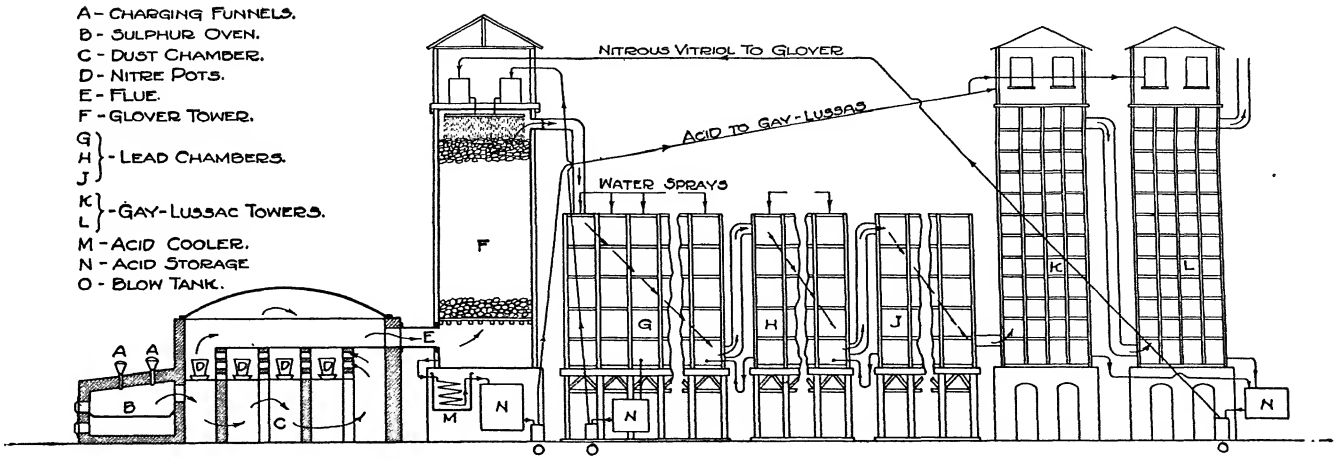


Fig. 38b. Diagram of Chamber Acid Process.

The first of these reactions may be expressed as follows:

$$2SO_2\begin{cases}ONO\\OH\end{cases} + H_2O = 2H_2SO_4 + N_2O_3,$$

and

$$N_2O_3 + SO_2 + H_2O = H_2SO_4 + 2NO,$$

or, adding these together,

$$2SO_2\begin{cases}ONO\\OH\end{cases} + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

The first portion of this reaction causes heat to be evolved, while the second portion, where N_2O_3 is reduced to NO, causes the absorption of heat, the formation of sulphuric acid in the tower therefore requiring that a temperature be maintained in the lower portion of from 150° to 160° C., 302° to 320° F., this temperature being necessary to decompose the nitrous sulphuric acid. The reactions in the upper portion of the tower, where the gases are liberated together with NO, may be expressed as

$$2NO + O = N_2O_3,$$

and

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\begin{cases}OH\\ONO\end{cases}$$

or together,

$$2SO_2 + 2NO + O_3 + H_2O = 2SO_2\begin{cases}OH\\ONO\end{cases}$$

These two reactions are exothermic, and they are greatly assisted by the gradual abstraction of the evolved heat, thus causing the formation of some additional nitrosyl-sulphuric acid, yielding sulphuric acid in the lower portion of the tower.

The vapors leave the Glover tower and enter the first lead chamber, being so regulated in their flow that the acid formed here has a concentration of 50° to 53° Bé.; in the last chamber, the train usually consisting of three, where no steam or water is injected, the gases are poor, and the acid may be as low as

40° Bé. About 75 per cent of the SO_2 coming from the Glover tower is converted into sulphuric acid in the first chamber, 20 per cent in the second, and 4.5 per cent in the third, the latter mainly acting to cool and dry the gas.

Sufficient steam or water spray must be admitted into the lead chambers to transform practically all of the SO_2 into sulphuric acid, this reaction concerning all the constituents except nitrogen.

The reactions in the lead chamber are very complex, and are not very well understood, but the equilibrium between the various reactions seems to depend upon the quantitative relation between the reacting substances, the temperature, and the volume of the lead chamber. It may be advanced, however, that nitrogen peroxide (NO_2), due to the loss of one atom of oxygen, will be reduced to nitric oxide (NO), and the latter in turn will unite with atmospheric oxygen and thus be reconverted into nitrogen peroxide, therefore, when sulphur dioxide, oxygen and nitrogen peroxide are mixed in the presence of water, the series of reactions which take place will lead to the formation of dilute sulphuric acid. The series of reactions which thus take place may be expressed as

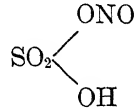
$$\begin{aligned} S + O_2 &= SO_2, \\ 3SO_2 + 2HNO_3 + 2H_2O &= 3H_2SO_4 + 2NO, \\ 2NO + O_2 &= 2NO_2, \\ 2NO_2 + 2SO_2 + 2H_2O &= 2H_2SO_4 + 2NO, \end{aligned}$$

but the theoretical interpretation of these reactions is still under continuous discussion.

The lead chambers are erected on an elevation above the ground, the floor of the chamber resting on a platform of wood. The walls and roof are also supported on a wood frame in order to supply a solid backing to the lead plates. The volume of the lead chambers must be large, because the yield will greatly depend upon properly mixing the gases; the first chamber is the largest, the other two decreasing in size.

Since nitrogen comprises about four-fifths of the air, it becomes necessary to provide some means for the escape of this nitrogen, and at the same time to prevent the escape of the oxides of nitrogen as far as possible, and for this purpose the chamber gases are caused to pass through the Gay-Lussac

towers. These towers are constructed entirely of lead, similar to the Glover tower, supported on a wooden frame; the bottom of the tower is set about 7 to 8 feet above the ground, the internal diameter being from 7 to 8 feet, with a height of from 25 to 30 feet. (Both the Glover and the Gay-Lussac towers are also built of a square cross-section.) The interior of the tower is filled with acid-resisting surface material, supported on lead gratings. The nitrous gases from the lead chamber enter the bottom of the tower, and are brought into intimate contact with sulphuric acid of 60° Bé. during the upward passage to the outlet, the acid being fed in continuous streams from a distribution system located under the roof at the top of the tower. This acid spray dissolves the nitrogen oxides contained in the gases, and forms the so-called nitrous sulphuric acid, this being a solution of nitrosyl-sulphuric acid, or



in sulphuric acid.

The acid used in the towers is collected in receivers of lead, stoneware, or cast iron, pressure pots, or Montejus, being used to raise the acid to the top of the towers by means of air pressure.

After the gases exit from the Gay-Lussac towers, they are practically purified from both SO_2 and oxides of nitrogen, and they are then finally exhausted through a stack into the air, a fan being sometimes located at this point to assist the draught.

From the foregoing it will be seen that sulphuric acid is formed by combining sulphur dioxide, oxygen, and water by means of the oxides of nitrogen, this acid being formed in the lead chambers, precipitated on the walls, and collected on the floor of the chamber. The acid in the last chamber is the purest, but also the weakest (48° to 50° Bé.) made in the system, and it can be taken directly from here and concentrated in a separate plant, whenever a purer and stronger acid than ordinary chamber acid is desired.

Under ordinary conditions, however, this acid flows forward into the second, or middle chamber, where it increases slightly in strength by union with the stronger acid made in this warmer chamber; due to the dust settling in this chamber the acid is,

however, slightly contaminated. From the second chamber the acid is fed to the first, where it reaches a strength of between 52° and 54° Bé. From here the product may be partly withdrawn for sale or use, or for concentration in a separate plant, or it can be taken direct to storage.

If the above procedure is not followed the acid may be elevated, by air pressure from Montejus, to the tank in the top of the Glover tower, where it is mixed with nitrous vitriol, thus concentrating it, but it will soon be diluted again from the steam condensed by the two cold acids. It also loses strength due to the conversion of any excess oxides of nitrogen or sulphur dioxide contained in it, and assists to liberate the lower oxides from their solution in the nitrous vitriol.

The nitric and nitrosyl-sulphuric acids are decomposed by coming in contact with the sulphur dioxide in the hot gases, and the resulting oxides of nitrogen are carried away with the gases leaving the Glover towers. The acid, as it trickles down through the filling material, receives further heat from the hot ascending gases, and it soon begins to give up water, thus becoming concentrated, and flowing from the tower into the coolers, reaching a strength of between 59° and 61° Bé. After being cooled, a portion of this strong acid is fed to the top of a second Gay-Lussac tower, where it descends and meets the outgoing gases, dissolving and recovering the final portions of nitrous gas not absorbed in the first Gay-Lussac tower. The acid flows from the bottom of this second Gay-Lussac and enters storage, and the excess of this circulating acid thus formed by the continuous addition of weaker nitrous vitriol, becomes the strong nitrous vitriol that is fed to the top of the Glover tower, and thus returns the recovered nitrous gases to the process.

The acid coolers consist of a wooden tank, divided into compartments, lined with lead, each compartment containing a series of lead pipe coils, the acid being fed into these coils by means of a silica funnel; the outlet end of the coil is brought to the top edge of the tank and ends in a trough leading to storage. The tank is kept full of moderately cold water, and the acid should not be admitted into the coils until they are cooled by the water.

The use of nitric acid in the Glover tower has worked out in practice to better advantage than when niter pots are used

in the oven, as the action of the niter pots is not as regular as feeding nitric acid to the tower, the latter method being under the complete control of the operator.

The 60° Bé. acid is usually stored in steel tanks, or tanks built of wood and lined with lead, and it can be shipped in tank cars, tank wagons, carboys, or drums.

If the acid is to be used for benzol washing, it will have to be concentrated, and it will therefore have to undergo a process of evaporation. The usual method of procedure in this case is to feed the acid into a cascade concentrating plant, this cascade arrangement consisting of a series of fused silica trays or basins, so set that the acid fed into the topmost basin overflows into the one directly below, and so on down the entire series. The heat applied under these basins slowly and gradually evaporates the water from the acid, and the latter thus becomes concentrated more and more as it descends the series of trays, finally entering pot-type coolers, from whence it flows into a lead cooler, where the temperature is reduced to that of the atmosphere, and then on into storage. The hot gases are drawn from the furnace to under the basins, and then pass out to a stack communicating with the atmosphere, while the acid fumes, due to evaporation, are drawn off in a separate flue and passed to a coke, or similar scrubber.

CHAPTER VII

TESTS

Test for Tar (Dry) in Coal Gas

To test for tar, estimated as dry tar, since no account is taken of the contained water in this instance, a tube such as shown in Fig. 39 is inserted in the gas main; this tube should be of such length as to permit it to project a sufficient distance into the gas main to avoid aspirating the skin of "dead" gas near the outer circumference of the main, this projection being usually from four to six inches, depending upon the diameter of the main.

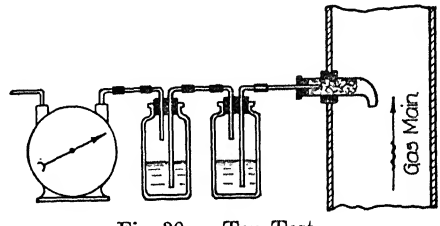


Fig. 39. — Tar Test.

The clean, dry tube, having a bore of about one-half inch, is packed with glass wool as shown, and after having been placed in a desiccator for from one to two hours, the tube with its contents is accurately weighed and the weight noted. In placing the tube in the main care must be taken to see that the one-eighth inch orifice at the end is directly in the current of gas, the outer end of the tube being connected to the two wash bottles and meter as shown, the one bottle containing H_2SO_4 for the absorption of NH_3, and the other containing NaOH for the absorption of H_2S.

After five or ten cubic feet of gas, the average temperature of which has been observed and noted at the meter, have passed through the apparatus, the glass test tube is connected to a Chapman or similar filter pump and the air, which is drawn through the H_2SO_4, is aspirated by means of the pump until a constant weight is secured, at least three weighings being necessary to determine this weight. Then

$$\frac{\text{Increase in Weight}}{\text{Corrected Gas Volume}} \times 100 = \text{grammes of tar,}$$

and this product multiplied by 15.432 will give the grains of tar per 100 cubic feet.

The $C_{10}H_8$ content of this tar may be determined by placing two (2) wash bottles containing picric acid solution between the tar tube and the pump, the estimation of naphthalene being then carried out according to the method described for the naphthalene test.

This method is one of usual practice, but Feld (see "Journal für Gasbeleuchtung," Jan., 1911) states that a gas saturated with fluid vapors at the temperature of saturation cannot absorb any more of these same vapors, and he based his method of tar determination on this principle, and proceeds as follows:

The gas, the tar content of which is to be determined, is led through a dry "U" tube filled with absorbent cotton, the exact weight of which is known, this "U" tube being kept at the same temperature as the temperature of the gas while the test is being run, so that the absorbent takes up as little water with the tar as possible. The drying of the tar in the "U" tube is accomplished through the heat contained in gas which has been freed of tar fog and water, at the same or at a slightly lower temperature; as this gas is saturated with the vapors of tar constituents, but is water free, it can absorb water vapors, but no vapors of tar constituents.

Fig. 40 shows the arrangement used by Feld; this consists of a rectangular, insulated vessel (*a*), the top being provided with the necessary plug holes in which three "U" tubes (*b*), (*c*), and (*d*) are inserted. The tubes (*b*) and (*d*) contain absorbent cotton (or glass wool), while (*c*) contains calcium chloride; the vessel (*a*) is filled with a liquid having a temperature equivalent to the one at which the tar test is to be run. The tube (*d*) is first dried until it has a constant weight, the gas used for drying leaving the gas main at tube (*e*) and entering the "U" tube (*b*), where it deposits all condensed tar constituents, then giving up its water content to the calcium chloride in (*c*), while in (*d*) the moisture contained in the cotton only is found.

After tube (*d*) has been dried to a constant weight, it is connected directly to the gas main by means of tube (*e*) and by by-passing tubes (*b*) and (*c*) a measured quantity of gas

is led through it, after which tube (*d*) is again connected to and behind tubes (*b*) and (*c*) and dry, tar-fog free gas is again drawn through it. During the test, as well as during the drying period, tube (*d*) is kept in the vessel (*a*) filled with warm water, and if the vessel (*a*) is well insulated the water temperature will remain constant during the test, but if necessary the warm water may be renewed from time to time through the medium of inlet (*f*) and outlet (*g*).

Owing to the fact that the gas retains its temperature while being passed through tube (*d*), the absorbed tar will contain but little water, and the drying process is therefore very rapid. Usually constant weight is secured in (*d*) as soon as a little

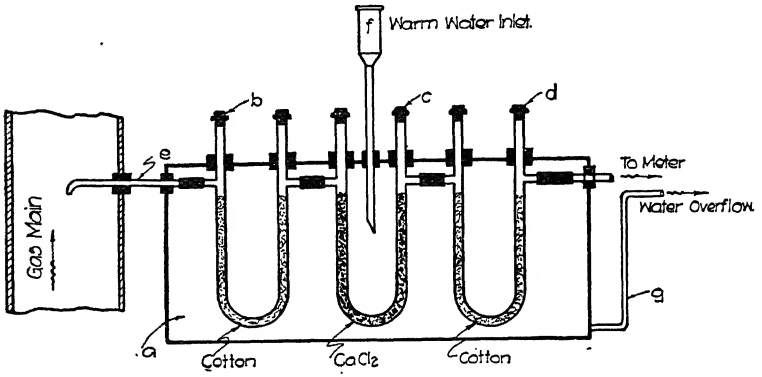


Fig. 40.—Feld Tar Test.

more gas is passed through for drying than was used for the analysis, and tubes (*b*) and (*c*) are refilled from time to time as required.

A tar test should either show the amount of tar fog remaining in the gas at a determined temperature and at a predetermined point, or the amount of tar constituents which will be separated from the gas by cooling to a certain temperature at a point behind, or after the point where the test is made. In the first case the temperature of the bath is maintained at the temperature of the gas to be tested, and in the latter case at the temperature to which the gas is to be cooled.

If, for example, the tar content of the gas is to be determined directly ahead of the Pelouze, and if the temperature

of the gas at this point is 20° C. (68° F.), the temperature of the bath should be maintained at 20° C., but if the test is to determine how much tar will be separated by cooling the gas from 60° to 30° C. (140° to 86° F.), the test should be made at a point where the temperature of the gas is 60° C., and the temperature of the bath should then be maintained at 30° C., but in the latter case the gas should be passed very slowly through the tubes, so that the temperatures may be equalized.

If it should be desired to determine the amount of tar fog present at 60° C., and how much tar oil or naphthalene will be separated during a drop in temperature from 60° to 20° C. (140° to 68° F.), two test tubes are placed behind each other, the first being maintained in a bath of 60° C. and the second in a bath of 20° C., while the drying process can be carried out without any difficulty at the lower temperature, because the gas at a lower temperature is always saturated with the tar constituents which would be separated at a higher temperature, but in no case should the drying be carried out at a higher temperature than the one at which the test is to be run.

Drying with gas consumes much less time than with air, and consequently Feld's method has been adopted to quite an extent in Europe.

Test for Naphthalene in Coal Gas:

In making a test for naphthalene in crude gas containing NH_3 and H_2S, wash bottle (*A*) containing a saturated solution of oxalic acid, and bottle (*E*) containing an NaOH solution, Fig. 41, are placed before and after the two bottles (*B*) and (*C*) containing picric acid as shown. Twenty-five cc. of picric acid solution is placed in each of the bottles (*B*) and (*C*), and the 250 cc. flask (*D*) should contain 75 cc. of the same solution, while the NaOH equivalent of this picric acid solution should be determined prior to each test, unless more than one test per day is made.

The glass tube, which in the case of crude gas should be filled with glass wool, is inserted into the gas main as shown, and from two to ten cubic feet of gas should be passed through the test, this volume depending upon the $C_{10}H_8$ content of the gas. After this volume of gas has been passed,

the test is disconnected and the bottles (*B*) and (*C*) washed into flask (*D*), sufficient picric acid being added from a pipette to make about 200 cc. of solution, after which the tube (*F*) is placed in the flask and connected to a Chapman pump, exhausting until all air bubbles cease to appear, after which the flask is sealed by pulling the glass tube up into the cork until the hole in the side of the tube no longer communicates with the flask. The flask is then placed in a water bath and boiled until all of the yellow crystals are dissolved.

The flask should then stand for from six to eight hours, or until the flask is cold, after which the volume is made up to 250 cc. with distilled water; the contents are then

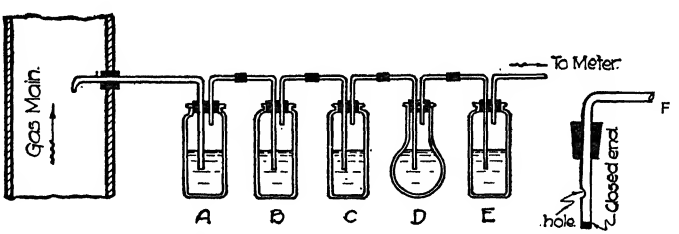


Fig. 41.—Naphthalene Test.

agitated by shaking the flask, after which the contents are filtered through a dry filter into a dry beaker. Take 25 cc. portions of the filtrate, using lacmoid as an indicator, and titrate with $N/_{10}NaOH$ until a final drop produces a green coloration.

One cc. of $N/_{10}NaOH$ is equivalent to 0.197 grain of $C_{10}H_8$, and if 175 cc. of the picric acid solution were used in the test, and if this is equivalent to "A" cc. of $N/_{10}NaOH$, and if the 250 cc. of filtrate is equivalent to "B" cc. of $N/_{10}NaOH$ then

$$\frac{(A - B)\ 0.197}{\text{corrected gas volume}} \times 100 = \text{grains of } C_{10}H_8 \text{ per 100 cubic feet of gas.}$$

It is very important that this test should be run and kept at the same temperature as that of the gas being tested, and this can best be done in the same manner as described in Feld's tar test.

Test for Ammonia in Coal Gas:

The standard solutions used in this test consist of standard HCl, Hydrochloric acid — 1 cc. = 0.5 grain NH_3, and standard NaOH, Sodium-hydroxide, 1 cc. = 1 cc. HCl = 0.5 grain NH_3; it is extremely important that these two solutions should exactly check each other, or that 1 cc. of NaOH should neutralize 1 cc. of HCl.

Ten cc. of the standard HCl solution, with sufficient distilled water to provide a seal of from one-half to three-quarters of an inch, should be placed in each of two gas-washing bottles, these bottles being connected to the sampling tube which should be inserted into the gas main for a distance of about four inches, depending upon the diameter of the main, using rubber tubing for sleeve connections but bringing the ends of the glass tubes together in the sleeves. A bottle containing a 20 per cent NaOH solution should be placed before the wet experimental meter to absorb any H_2S, as shown in Fig. 42, after which gas is passed through the solutions at the rate of one-half to three-quarters of a cubic foot per hour, the meter reading and the temperature of the gas leaving the meter being accurately ascertained and noted.

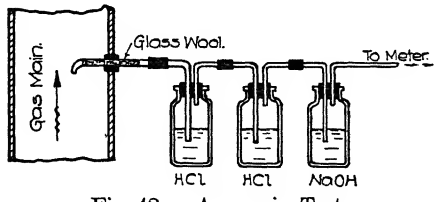


Fig. 42. — Ammonia Test.

Prior to the ammonia scrubber, the passing of one cubic foot of gas through the solutions will be sufficient for the test, but after the scrubber about five cubic feet should be run through the bottles, the latter test being so regulated that both tests will be run at the same time, these tests being for the purpose of determining the amount of ammonia removed from the gas in the scrubber.

If much tar is present in the gas, the sampling tube leading to the wash bottles should be packed with glass wool in order to prevent the tar entering the bottles.

After sufficient gas has been passed, the bottles are disconnected, the contents washed into a clean beaker of at least 250 cc. capacity, a few drops of lacmoid indicator added, and enough of the standard NaOH solution run in from a

burette, so that a final drop of this solution causes a faint blue coloration of the liquid, indicating that the end point is reached, the solution being constantly stirred during titration.

The following calculation will give the quantity of ammonia in the gas thus tested:

Amount of standard HCl used	20 cc.
" " NaOH for titration, say	14 cc.
" " HCl combined	6 cc.
Gas registered by test meter	1.00 cu. ft.
Temperature of gas at outlet of meter	75° F.
Corrected volume: 1.0 × 0.960	0.96 cu. ft.

then

$$\frac{6 \div 2}{0.96} \times 100 = 312.5 \text{ grains per 100 cubic feet, or}$$

$$\frac{\text{Excess} \div 2}{\text{Corrected gas volume}} \times 100 = \text{grains per 100 cubic feet.}$$

In order to make a standard sodium carbonate solution, take 55 grammes of dry Na_2CO_3, C.P., and place it in a clean porcelain or platinum crucible and heat gently, weighing from time to time until the weight becomes constant, or until no further loss in weight is noted. This heating is best accomplished by placing the crucible on a bent triangle and placing the latter on wire gauze (Fig. 43), as the crucible should only show a dull glow on the bottom.

When the weight has become constant take *exactly* 50.330 grammes of the carbonate and place it in a 500 cc. stoppered volumetric flask, then add distilled water to the mark on the flask.

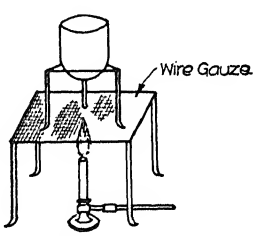


Fig. 43.—Ammonia Test.

To prepare the standard HCl or hydrochloric acid solution in which 1 cc. = 0.5 grain of NH_3, place about 160 cc. of C.P. hydrochloric acid of 1.19 to 1.20 specific gravity and containing 37.5 per cent HCl (absolute) in a liter flask, and add enough distilled water to fill to the mark on the flask.

After being well shaken, a clean burette is filled with this solution and enough of it is run into a beaker, the latter containing 25 cc. of the sodium carbonate solution and a few

drops of methylorange, the latter as an indicator, until a final drop from the burette causes a red coloration which remains permanent for one-half minute.

If it requires 24.5 cc. of HCl for 25 cc. of Na_2CO_3, then each 980 cc. of the HCl must be diluted to 1000 cc., as $24.5 \times 40 = 980$ cc. equal to 1000 cc. Na_2CO_3, and the dilution is necessary as 1 cc. HCl should exactly equal 1 cc. of Na_2CO_3 solution.

After dilution, clean out burette and fill with the diluted solution, titrating as before until 25 cc. of HCl neutralizes 25 cc. of Na_2CO_3 solution.

To prepare a standard NaOH solution, dissolve 80 grammes of C.P. caustic soda in sufficient distilled water to make 1000 cc. With a pipette place 25 cc. of this solution in a beaker and run in the standard HCl solution, using lacmoid as an indicator, until a final drop produces the end point; as it will probably require more of the HCl to neutralize, it will be necessary to dilute, as in the former case.

Then the number of cc. of HCl $\times$ 40 = number of cc. to which 1000 cc. NaOH solution must be diluted, or $25.6 \times 40 = 1024$ cc., or each 1000 cc. must be diluted to 1024 cc. with distilled water.

After a thorough mixing, the solutions should be checked until they both agree in strength, and as the accuracy of all tests depends upon the solutions, a great deal of care should be exercised in their manufacture; the sodium carbonate (Na_2CO_3) is the starting point, and if that is not just what it should be the other two solutions will also fail. The carbonate should be well dried and not heated too high, otherwise the salt will lose CO_2, and the HCl and NaOH *must* exactly check.

Test for Cyanogen in Coal Gas:

In testing for cyanogen, as practised in the United States, the following solutions are used:

Ferrous sulphate ($FeSO_4.7H_2O$) .....10% Solution

Sodium hydroxide (NaOH) or Potassium hydroxide.....20% Solution.

Zinc sulphate ($ZnSO_4$), standard solution, the value of each cc. in terms of $(CN)_2$ must be known.

Ferric alum in a 2 per cent solution is used as an indicator.

Into each of three gas-washing bottles place 15 c.c. of the $FeSO_4$ solution and 15 c.c. of the KOH solution, and shake well to prevent the formation of lumps; then add sufficient distilled water to provide a one-inch seal for the gas inlet tubes.

Pass from 3 to 5 cubic feet of gas through the bottles, and then wash the contents of the bottles into a suitable casserole, being careful to remove all insoluble matter, and boil until no more NH_3 is evolved, testing for this result with turmeric paper; wash the hot solution into a graduated volumetric flask, cool, and make up to the mark on the flask with distilled water, shake well and then filter through a dry filter.

Place 50 or 100 c.c. portions of the filtrate in a beaker, and acidify to slightly acid reaction with dilute H_2SO_4; then add an excess of 10 c.c. of dilute acid, and titrate with the standard zinc solution until a final drop placed in proximity to a drop of the ferric alum solution on Schleicher and Schul drop reaction paper No. 601 shows no blue zone at the point of contact, care being taken that the iron solution does not touch the inner circle of the test drop. Then

$$\frac{\text{Total c.c. zinc used} \times \text{equivalent } (CN)_2 \text{ per c.c.} \times 100}{\text{corrected gas volume}} = \text{grains}$$

per 100 cubic feet.

To standardize the zinc solution, which may be made up by dissolving say 16.5 grammes of zinc sulphate C.P. in 1000 c.c. of distilled water, a 1 per cent solution of potassium ferro-cyanide, $K_4Fe(CN)_6$, C.P., made with clear yellow crystals, is utilized. Twenty-five c.c. portions of this solution are made up to 100 c.c. with distilled water and acidified with dilute H_2SO_4, and after the addition of 10 c.c. more dilute acid, the solution is titrated with the zinc solution until a final drop does not produce the blue zone in contact with the drop of indicator. It is essential that the same conditions as to volume and acidity be observed on both standardization and test titrations. Dividing the equivalent of the 25 c.c. in terms of the potassium ferro-cyanide by the number of c.c. of zinc solution used, will give the value of each c.c. of zinc solution in terms of potassium ferro-cyanide, and multiplying this result by 0.3695 and again by 15.432 will give the equivalent of 1 c.c. $ZnSO_4$ solution in grains of cyanogen.

Determination of prussian blue in Cyanogen:

The method devised by Feld to determine the "blue" content of cyanogen seems to give a simple, sure, and rapid analytic process for the use of those chemists who are compelled to analyze either spent oxide or cyanogen sludge and to determine its value based on "blue" content.

Feld showed (see "Journal für Gasbeleuchtung," 1904) by a great many tests that the loss in cyanogen through the formation of sulphocyanides is very large when the methods of analyses devised by Moldenhauer and Lybold, as well as Knublauch are used, due to the decomposition of the cyanogen in contact with caustic potash. He further claims that the method of Drehschmidt does not entail these losses, but that the conversion of cyanogen combinations into mercuric cyanide is a very slow process, and therefore leads to discrepancies.

Table XIX gives the results of an examination of twelve samples of spent oxide according to Feld's method, and to the combined method of Knublauch and Drehschmidt as recommended by Burschell and Lubberger. This combination analysis — breaking up cyanogen combinations with caustic potash, separating the "blue" therefrom, decomposing the latter with mercuric oxide, and transposition into ammonium cyanide and sodium cyanide, and then titrating the latter according to Volhard — has to a great extent displaced the individual methods of both Knublauch and Drehschmidt. This combination method gives results which generally coincide with the Knublauch method, although the values are somewhat higher, but it is also subject to the danger of sulphocyanide formation by long contact with the caustic potash, while on the other hand the conversion of the pure, fine-particled "blue" into mercuric cyanide through boiling for fifteen minutes with mercuric oxide can be thoroughly accomplished without any loss.

It is however, of extreme importance, after the "blue" has been washed out, and during the remainder of the analysis, to use only such reagents as are free from chlorine, otherwise the result of the titration will be too high, and the chemist is cautioned that the zinc dust used to decompose the mercuric cyanide often contains chlorine which is difficult

TABLE XIX. — "BLUE" CONTENT OF SPENT OXIDE

	According to Feld			According to Knublauch-Drehschmidt			
No.	Value %	Difference	Average value %	Value %	Difference	Average value %	Difference as compared with Feld. %
I	9.106 9.106	.. 0.000	.. 9.106	9.09 8.88	.. 0.21	.. 8.985	.. −0.121
Without Cyanogen Alkalies	8.869 8.715	.. 0.154	.. 8.792	.. ..	.. ..	.. ..	.. ..
II	9.164 9.221	.. 0.057	.. 9.193	8.89 8.72	.. 0.17	.. 8.805	.. −0.388
Without Cyanogen Alkalies	8.978 8.954	.. 0.024	.. 8.966	.. ..	.. ..	.. ..	.. ..
III	10.062 10.120	.. 0.058	.. 10.091	10.08 9.88	.. 0.20	.. 9.980	.. −0.111
Without Cyanogen Alkalies	10.043 10.081	.. 0.038	.. 10.062	.. ..	.. ..	.. ..	.. ..
IV	7.931 7.931	.. 0.000	.. 7.931	7.38 7.33	.. 0.05	.. 7.355	.. −0.576
V	8.959 8.897	.. 0.062	.. 8.928	8.00 8.00	.. 0.00	.. 8.000	.. −0.928
VI	8.812 8.812	.. 0.000	.. 8.812	8.20 7.92	.. 0.28	.. 8.060	.. −0.752
VII	8.100 8.188	.. 0.088	.. 8.144	7.66 7.67	.. 0.01	.. 7.665	.. −0.479
VIII	8.615 8.591	.. 0.024	.. 8.603	7.98 7.90	.. 0.08	.. 7.94	.. −0.663
IX	8.725 8.772	.. 0.047	.. 8.748	8.23 8.25	.. 0.02	.. 8.24	.. −0.508
X	9.040 8.963	.. 0.077	.. 9.002	8.43 8.43	.. 0.00	.. 8.43	.. −0.572
XI	9.470 9.527	.. 0.057	.. 9.499	9.29 9.29	.. 0.00	.. 9.29	.. −0.209
XII	8.925 8.925	.. 0.000	.. 8.925	8.68 8.68	.. 0.00	.. 8.68	.. −0.245

to remove. As a whole, this method requires the utmost care, is rather difficult to carry out, requires a great deal of time, and, as stated before, does not give results which cannot be disputed.

The simplicity and rapidity of Feld's method has therefore found much favor in Europe, especially as a method for forming the basis of all analysis for the sale of the "blue," where disputes so often arise between the chemist of the producer and the one employed by the purchaser.

The principle upon which this method of Feld's is based consists in separating the cyanogen in the form of hydrocyanic acid (HCN) from its various combinations by distillation, its absorption in a sodium solution, and the direct determination of the resultant sodium cyanide with a nitrate of silver ($AgNO_3$) solution.

In order to prevent the iron cyanide combinations being transformed into sulphocyanides during the analyses, the separation of the cyanogen $(CN)_2$ with caustic potash must be done in a cold atmosphere and in the shortest possible time, and the further action of the caustic must be neutralized by adding magnesium chloride ($MgCl_2$) before heating. The formation of sulphocyanides is thus totally obviated. Due to an excess of magnesium chloride solution all free caustic is converted into chloride with the separation of magnesium hydroxide, and ammonia and hydrogen sulphide are soon liberated by boiling:

$$K_2S + MgCl_2 + 2H_2O = Mg(OH)_2 + 2KCl + H_2S,$$

or the addition of magnesium chloride and water to the potassium monosulphide, forms magnesium hydroxide and potassium chloride with the liberation of hydrogen sulphide.

Thereupon the iron cyanide combinations are decomposed with a mercuric chloride solution, from which, due to the excess of magnesium chloride and in spite of the alkalinity of the solution, no mercuric oxide is separated, but mercuric cyanide is produced with a separation of ferric hydroxide, or

$$2K_4Fe(CN)_6 + 8HgCl_2 + 3Mg(OH)_2 = 6Hg(CN)_2 + Hg_2Cl_2 + 2Fe(OH)_3 + 8KCl + 3MgCl_2.$$

The complete decomposition is indicated by a light brownish-red precipitate in the clear liquid. The excess of

the amount of magnesium chloride over that equivalent to the alkali should be such that from 3 to 4 molecules of $MgCl_2$ should be present for each molecule of $HgCl_2$, because with a less amount mercuric oxide, or basic mercury salts, is separated, retarding the transposition into mercuric cyanide.

The solution of mercuric chloride must be added to the boiling iron cyanide solution in a boiling condition, since if one of the solutions should not be hot enough, mercuric ferro-cyanide, which is difficult to decompose, will be formed.

The HCN is liberated from the mercuric cyanide by distilling with dilute sulphuric acid, absorbing it in a dilute sodium solution.

As an indication of incomplete decomposition while boiling with the mercuric chloride solution, a blue discoloration will appear after the acid has been added, due to the action of the iron sulphate on the mercuric ferro-cyanide. Traces, which always escape during any process of decomposition, will give the distillation residual a dirty-green color. The excess of acid, after the removal of the amount equivalent to the alkali present, must be equivalent to at least four to five times the added mercuric chloride.

During distillation sulphur, evolved from free sulphur or from polysulphides, also passes over and dissolves in the sodium solution forming sulphide or thiosulphate, and thus disturbs the titration with the silver solution, but the addition of about 0.5 gramme of lead carbonate solves this difficulty.

According to whether the total cyanogen, or only that part which is in combination with iron, is to be determined, the free alkaline cyanide is either transformed into iron cyanide by the addition of iron sulphate,

$$6NH_4CN + 6NaOH + FeSO_4 = Na_4Fe(CN)_6 + Na_2SO_4 + 6NH_3 + 6H_2O,$$

or the cyanogen contained in the potassium cyanide is liberated by heating with magnesium chloride:

$$2KCN + MgCl_2 + 2H_2O = Mg(OH)_2 + 2KCl + 2HCN.$$

Feld recommends that a few c.c. of potassium iodide be added for the titration of the sodium cyanide with the silver

solution, and states that the titration will be correct even though chlorides are present.

The apparatus recommended by Witzeck for this analysis is shown in Fig. 44.

The solution to be distilled is placed in the flask (*A*) having a capacity of 700 c.c. A dropper (*B*) combined with the Leibig condenser (*C*) is passed into the flask through a rubber stopper on the one side, and a funnel (*D*) with a glass cock on the other side, this funnel serving to admit the sulphuric acid. The condenser terminates in a flask (*E*) containing the sodium solution, this flask also being

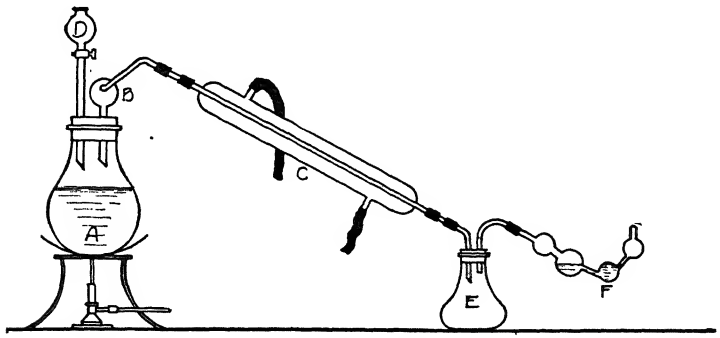


Fig. 44. — Feld "Blue" Test.

connected to a safety tube (*F*) comprising three bulbs, the latter also containing sodium solution.

The total cyanogen in spent oxide, or in cyanogen sludge, is then determined as follows:

Two grammes of the mass (or 0.5 gramme of sludge) are placed in a mortar and 1 c.c. of $2/_{N}FeSO_4.7H_2O$ solution (278 grammes of iron vitriol per liter) is added together with 5 c.c. of $8/_{N}NaOH$ (320 grammes per liter). This is pestled for five minutes, and then 50 c.c. of $6/_{N}MgCl_2$ solution (610 grammes per liter) is slowly added, the mixture being constantly stirred, after which the entire mass is washed with hot water into the distilling flask (*A*), sufficient hot water being added to make up about 200 c.c.; after boiling about five minutes, 100 c.c. of boiling $N/_{5}HgCl_2$ solution (27.1 grammes of sublimate per liter) is added to the mixture, and then boiled again for ten more minutes, after which flask (*A*)

is connected to the condenser, 30 c.c. of $8/_{N}H_2SO_4$ (392 grammes per liter) are added, and then distilled for from 20 to 30 minutes; flask (*E*) is supplied with 20 c.c. of $2/_{N}NaOH$ (80 grammes per liter). If the distillate is turbid, 0.5 gramme of lead carbonate is added to the measuring flask to which it has been transferred.

Aliquot portions of the solution, after the addition of 5 c.c. of $N/_4KI$ (41.5 grammes per liter) are titrated with $N/_{10}AgNO_3$, the end point being indicated by the formation of a yellowish-milky turbidity. One c.c. of $N/_{10}AgNO_3$ (17.0 grammes per liter) is equivalent to 0.009548 gramme of "prussian blue," $Fe_7(CN)_{18}$.

DETERMINATION OF BENZENE, TOLUENE, AND SOLVENT NAPHTHA IN LIGHT OILS

Method of D. Wilson and I. Roberts, Laclede Gas Light Company, St. Louis, Mo.

2100 c.c. of the crude oil is placed in a 2500 c.c. separatory funnel, and 100 c.c. of sulphuric acid (1.84 specific gravity) is slowly added. If much heating should take place, the acid should be added a little at a time, and thoroughly mixed with the oil by shaking for about one minute after each addition. The mixture of oil and acid should not be cooled unless the container becomes uncomfortably warm, and in that case it should be cooled only to about 50° C. (122° F.), as a warm temperature is especially conducive to good and quick separations when working with oils which are liable to heat very much; oils of this character also will create considerable pressure in the vessel and this condition should be relieved every few seconds by inverting the container and opening the stopcock.

After all the acid has been added, the mixture is agitated thoroughly for five minutes and then allowed to stand for fifteen minutes, in order that the acid tar may settle out. At the end of this period the sludge is carefully drawn off into a beaker of water, and if it partially dissolves in the water, forming a muddy solution, sufficient acid will have been added to destroy the olefines; if the sludge sinks to the bottom without mixing with the water, a second 100 c.c. of acid must be added, and the above procedure repeated. This acid treatment must be repeated until the sludge partially dissolves in the water. If

any oil should follow the sludge, it can be blown off into a small separatory funnel, the water can be drawn off, and the oil then returned to the main sample. After the final acid treatment, a little water is poured down the side of the container, allowed to settle, and is then drawn off, thus removing the small amount of sludge remaining in the bottom.

200 c.c. of warm sodium hydroxide solution (1 to 10) is now added, and the mixture is thoroughly agitated for five minutes. This should change the oil to a lighter color, but if this change fails to appear, a little more of the hydroxide should be added. The mixture is now allowed to settle until a clean-cut separation between the oil and the hydroxide appears, after which the hydroxide is carefully drawn off.

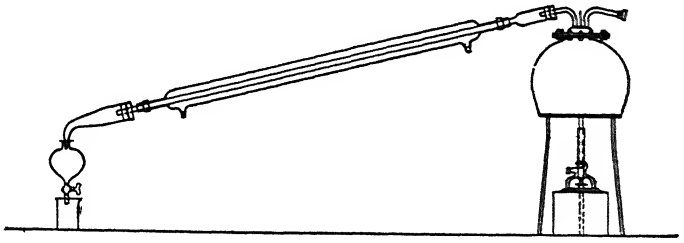


Fig. 44a. — Apparatus for Live Steam Distillation.

This washed oil is now placed in the one-gallon copper still, fitted for live steam distillation, Fig. 44a; this still is connected to a Liebig condenser having a 30-inch jacket, ending in an adapter on the lower end of the condensing tube. The washed oil is heated in the still to the boiling point by means of a small burner underneath, and a slow current of steam is then turned into the still. (One half-gallon still, fitted with a large riser to permit of draining back any condensation, will furnish sufficient steam for this distillation.) Distillation is continued until the flow of oil practically ceases, and the temperature of the vapors leaving the still will gradually rise to 100° C. (212° F.) before the distillation is finished. If a small flame is maintained under the steam still during distillation, it will prevent the condensation of much steam in the still, and also increase the rate of distillation. The distillate is collected in the same vessel as was used for the acid treatment, and the water is drawn off when necessary. When the distillation is

completed, the remaining water is carefully drawn off, and the oil is measured at the original temperatures.

The oil is now dried by passing it through the calcium chloride dryer (Fig. 44b), and $\frac{2}{2}\frac{0}{1}$ of its volume (measured at the same temperature) is placed in the copper flask of the fractional distillation apparatus. The calcium chloride dryer consists of a 1-inch by 30-inch tube, the bottom of the tube containing glass wool, the remainder of the tube being filled with fresh granular calcium chloride.

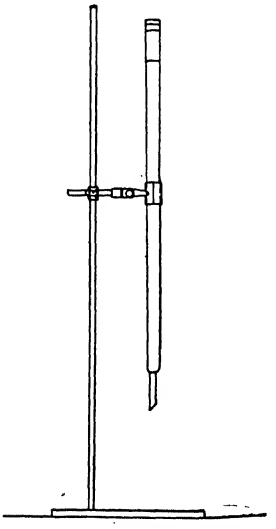


Fig. 44b. — Calcium Chloride Dryer.

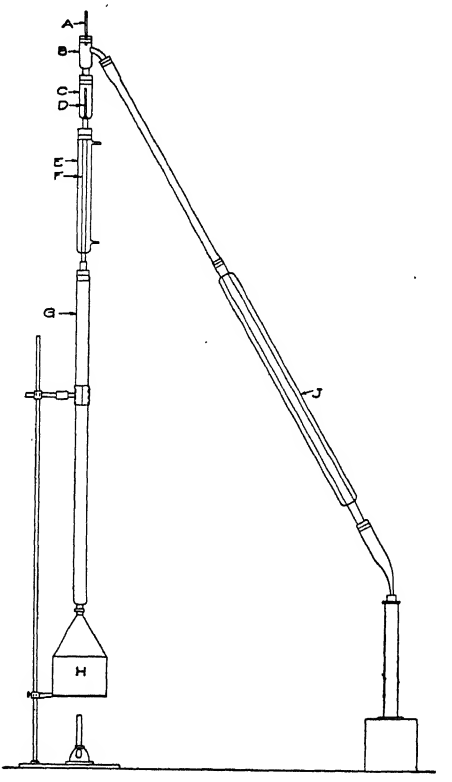


Fig. 44c. — Fractional Distillation Apparatus.

The fractional distillation apparatus for benzene, toluene, and solvent naphtha is shown in Fig. 44c. A 2200-c.c. copper flask (*H*) is fitted with a 40-inch Hempel column (*G*) having an inside diameter of 1 inch and filled with $\frac{1}{4}$-inch glass balls for 36 inches of its length. Attached vertically to the top of the Hempel column, is a 21-inch Liebig condenser tube (*C*), with the enlarged end up, this tube having an inside diameter of

½ inch. The condenser tube is supplied with an open-top Liebig condenser or dephlegmator jacket, 14 inches long (*E*), and is fitted inside with a sealed tube (*F*), ⅜ inch by 16 inches outside, set concentrically by means of vertical wires or by protuberances on the tube itself. The top of the condenser tube is fitted with a side-neck connecting tube (*B*), the delivery tube of which is bent down, and connected to a Liebig condenser (*J*) with a 30-inch jacket set almost vertical. An extra long condenser tube, with an adapter on its lower end, is used, thus bringing the distillate down to a convenient place for changing the receivers. The top of the apparatus is supplied with a ⅓-inch thermometer (*A*), and the condenser jacket is provided with a dephlegmator thermometer (*D*).

All vapor temperatures are measured with a certified gas-filled Centigrade thermometer, which is scaled for 3-inch immersion, and has a range of 75° to 150° C. (167° to 302° F.) in one-fifth degrees. The graduations start about one inch from the immersion line, so as not to be covered by the cork, and run about forty to the inch. All thermometers used for any of the distillations are set with the immersion line at the bottom of the cork, and the top of the bulb not higher than the bottom of the side-neck opening. All volumetric measurements are made in stoppered cylinders at a temperature of 20° C. (68° F.).

A Jena side-neck flask is used for distilling off the desired portion of the naphtha remaining in the copper flask at the end of the distillation period, a 12-inch Liebig condenser and a 3-inch immersion certified thermometer, graduated in single degrees, being used for this purpose.

The intermediates and known mixtures are tested in a 50-c.c. Jena side-neck flask connected to a Liebig condenser having a 12-inch jacket, and set at an angle of about 30° from the horizontal, the lower end of the condenser tube being provided with an adapter, while the temperatures are taken with the one-fifth degree thermometer. The measuring cylinder is graduated in 0.2 c.c.

The oil is purified in a 2500-c.c. separatory funnel, or in a half-gallon aspirator bottle with a glass stop-cock inserted in the upper stopper.

In order to prevent excessive distillation losses, the following precautions should be taken: (1) While making tests, all con-

densers and receivers in use should be cooled to at least 15° C. (59° F.). (2) Extra select corks should be used for connections. (3) While the distillate is being collected, a damp cloth should be wrapped around the adapter and the receiver opening in order to prevent the circulation of air.

If the fractional distillation apparatus is new, it will be best to boil some solvent naphtha in the copper flask, until the whole column is filled with vapors, then cool the flask with water and allow the column to drain for 15 minutes, thus practically eliminating the error that would otherwise be due to oil remaining in the column.

After the washed oil has been placed in the copper flask, the latter is connected tightly to the column, the dephlegmator jacket is filled with water, and the flask is slowly heated. After the oil begins to boil, the condensation in the column will be rapid, and it may fill up with liquid, in which case the burner should be withdrawn just long enough to allow the column to drain. As soon as the distillate begins to come over, the rate should be regulated to one drop each second.

The first runnings are taken off up to 79° C. (corrected) or 174° F. As benzene will at times come over below this temperature, due to a small amount of water in the oil, it is best to test this fraction for paraffins. The amount absorbed then can be added to the benzene percentage. The rate is now increased to 5 c.c. per minute, and the temperature will soon become stationary (80°–80.5° C. or 176°–177° F.) and remain so until most of the benzene is over. As soon as the temperature begins to rise again, the rate is again decreased to one drop a second until 81° C. (corrected) (178° F.) is reached, when the benzene fraction is taken off. Up to this point, the water leaving the dephlegmator should be kept at a temperature well below 80° C. (176° F.), but high enough to permit the distillation to take place at the stated rate.

The next fraction, which Wilson and Roberts call the B-T intermediate, is distilled at the rate of one drop a second, the dephlegmator water supply is shut off, and as soon as the water boils it is quickly drawn off and replaced with a hot solution of calcium chloride having a boiling point of 105° C. (221° F.). This fraction is taken off when the temperature reaches 109° C. (corrected) (228° F.).

Toluene now comes over, and while it is being collected the rate is increased to 5 c.c. a minute after having wrapped the Hemple column in asbestos paper. The temperature will soon become constant around 110.5°–111° C. (231°–232° F.), and when it starts to rise again the rate is decreased to one drop a second, and the fraction is taken off when the temperature reaches 111.5° C. (corrected) (233° F.).

The calcium chloride solution is now removed from the dephlegmator, the remainder of the column is wrapped in asbestos paper, and the distillation is continued at the rate of one drop a second until 137° C. (corrected) (247° F.) is reached, when the distillation is stopped. The condenser is allowed to drain and the T-S intermediate is taken off.

The asbestos wrappings are now removed, the copper flask is cooled with water, and the column is allowed to drain for 15 minutes. The naphtha remaining in the flask may be measured or distilled off to any desired temperature in the Jena side-neck flask. The distillation loss should not exceed one or two per cent, and this can be proportionately added to the various constitutents if the content percentage of the oil is desired.

The intermediates can be taken at the average figures of two-thirds of benzene to one-third of toluene, and two-thirds of toluene to one-third of xylene, or their composition can be determined as described below, and the amounts of benzene, toluene, and solvent thus found is added to their respective fractions.

To test the intermediates, 20 c.c. are distilled in the 50 c.c. side-neck flask at the rate of one drop each second. The corrected temperature is noted when the first drop falls into the measuring cylinder, and also the percentage off at the even degrees (corrected), *i.e.*, 86, 88, 90, etc., and 114, 116, 118, etc. Known mixtures are also distilled in the same way, and a permanent table is thus prepared. The composition of the intermediates can then be determined very closely by comparison. The following benzene-toluene and toluene-xylene mixtures will cover most intermediates: 60/40, 65/35, 70/30, 70/25.

The oils for preparing these mixtures can be obtained by distilling some of the pure oils in the fractionation apparatus; the benzene and toluene should be taken off while the temperature remains constant, and the xylene between 137° and 140° C.

(279° and 284° F.). If the intermediate should be less than 20 c.c., toluene (prepared as above) is added to make 20 c.c., and due allowance must later be made for this addition. The 50-c.c. flask should be supported by a 6-inch square of asbestos board about $\frac{1}{8}$ inch thick, this asbestos being provided with a 1-inch diameter hole in the center.

The steam distillation may be omitted if desired, in which case the oil should be measured after the washing with sodium hydroxide. The naphtha residue from the fractional distillation is distilled to the desired temperature, and the oil remaining in the flask is measured.

A low rate of distillation is desirable as the temperature rises to 81° and 111.5° C. (178° and 236° F.), thus assisting to produce small intermediates.

In order to correct for the effect of barometric pressure, the following fractional degrees should be added or subtracted for each mm. of pressure above or below 760 mm. respectively:

81° C. (178° F.)	0.043
109° and 111.5° C. (228° and 236° F.)	0.047
137° C. (247° F.)	0.052
Benzene-toluene intermediate	0.045
Toluene-xylene intermediate	0.050

By starting with less than 2200 c.c. and using a smaller copper flask, the time of distillation can be cut proportionately, but the fractionating efficiency will remain the same in either case; however, unless the oil contains at least 8 per cent of solvent naphtha, it will be best to start with more than 1000 c.c. of the crude oil, as about 70 c.c. of naphtha are required to send the T-S intermediate over.

Sample Distillation.

	Per cent	
Oil after steam distillation	93.3	
Up to 79° C. (174° F.)	0.2	
(due to water)		
81° C. (178° F.)	44.7	
109° C. (228° F.)	2.4	85.15
(exceptional)		
111.5° C. (236° F.)	37.1	
137° C. (247° F.)	2.0	65.35
Residue (solvent naphtha)	6.5	
Distillation loss	0.4	

Summing up, and eliminating the loss, we have:

	Per cent	
Benzene	0.2	
	44.7	
	2.0	
	0.2 (loss)	
	47.1	47.1%
Toluene	0.4	
	37.1	
	1.3	
	0.2 (loss)	
	39.0	39.0%
Solvent naphtha	0.7	
	6.5	
	7.2	7.2%
Olefines, etc		6.7%
		100.0%

As the specific gravity of benzene at 15° C. (59° F). is very close to 0.88, and that of toluene and solvent naphtha close to 0.87, specific gravities lower than these figures would indicate paraffins. These can be tested for as follows:

10 c.c. of oil to be tested are carefully measured into a 110-c.c. flask (with 10 c.c. graduations in tenths on the neck) and 25 c.c. of a mixture containing two parts by weight of sulphuric acid (sp. gr. 1.84), with one part of fuming sulphuric acid (20 per cent), are added; this mixture is agitated thoroughly for several minutes, and then allowed to stand for half an hour. The volume is then made up to nearly 110 c.c. by pouring concentrated sulphuric acid down the side of the flask. After being allowed to stand for an hour, the paraffins can be read off.

The advantages to be secured with this method, and with the apparatus developed for the purpose, are:

(1) The benzene and toluene produced will distill within 1.5° C. when tested in a side-neck distillation flask.

(2) The intermediates will average 25 c.c., and should not exceed 40 c.c.

(3) One fractional distillation will give the percentage of benzene, toluene, and solvent naphtha within a few tenths of 1 per cent.

(4) If the distillation is carried straight through at a rate not exceeding one drop a second, the benzene and toluene

produced will distill 97 per cent within one degree, the intermediates remaining the same as above.

C. P. GRADES

Benzol Specifications. No standard specifications for benzol and its homologues have as yet been adopted in this country, but the following are used by the larger dealers in these products:

Pure Benzol. Under this specification 100 per cent of the material shall distill entirely within a range of 2° C., and in which range shall be included the true boiling point of benzol. When three parts of the benzol are shaken with one part of C.P. sulphuric acid and allowed to stand for fifteen minutes, the benzol shall remain colorless and the acid may be slightly colored.

Pure Toluol. 100 per cent of the material shall distill entirely within a range of 2° C., in which range shall be included the true boiling point of toluol. When three parts of the toluol are shaken with one part of C.P. sulphuric acid and allowed to stand for fifteen minutes, the toluol shall remain colorless and the acid may be slightly colored.

COMMERCIAL GRADES

90 Per Cent Benzol. 90 to 93 per cent shall distill below 100° C.; specific gravity at 15.5° C. about 0.88. Color, water white. In sulphuric acid wash test only very slight color shall be imparted to acid (1.5 bichromate scale).

50 Per Cent Benzol. 50 per cent shall distill below 100°, 90 per cent below 120° C.; specific gravity about 0.88. Color, water white. In sulphuric acid wash test only slight yellow color shall be imparted to acid.

Toluol. 90 per cent shall distill between 100 and 120° C.; specific gravity about 0.87. Color, water white. In sulphuric acid wash test only slight yellow color shall be imparted to acid.

Solvent Naphtha. Distillation does not begin below 120° C. and 90 per cent distills below 160°; specific gravity about 0.87 to 0.88. Color, water white to slightly yellow. Sulphuric acid colored slightly yellow by wash test.

APPENDIX

TABLE XX. — COEFFICIENTS FOR VOLUME CORRECTION TO 60° F. OF GAS MEASURED AT DIFFERENT TEMPERATURES

Temperature	Coefficient	Temperature	Coefficient
40	1.050	69	0.977
41	1.049	70	0.974
42	1.045	71	0.971
43	1.042	72	0.968
44	1.040	73	0.966
45	1.038	74	0.963
46	1.035	75	0.960
47	1.032	76	0.958
48	1.030	77	0.955
49	1.028	78	0.952
50	1.025	79	0.949
51	1.022	80	0.946
52	1.020	81	0.944
53	1.018	82	0.941
54	1.015	83	0.938
55	1.013	84	0.935
56	1.010	85	0.932
57	1.008	86	0.930
58	1.005	87	0.927
59	1.003	88	0.924
60	1.000	89	0.922
61	0.997	90	0.919
62	0.995	91	0.916
63	0.993	92	0.913
64	0.990	93	0.910
65	0.987	94	0.907
66	0.985	95	0.905
67	0.982	96	0.902
68	0.979	97	0.900

TABLE XXI. — SPECIFIC GRAVITY OF AMMONIUM SULPHATE SOLUTIONS AT 15° C. (59° F.) (SCHIFF)

Specific Gravity	Percentage $(NH_4)_2SO_4$	Specific gravity	Percentage $(NH_4)_2SO_4$	Specific Gravity	Percentage $(NH_4)_2SO_4$
1.0057	1	1.1035	18	1.2004	35
1.0115	2	1.1092	19	1.2060	36
1.0172	3	1.1149	20	1.2116	37
1.0230	4	1.1207	21	1.2172	38
1.0287	5	1.1265	22	1.2228	39
1.0345	6	1.1323	23	1.2284	40
1.0403	7	1.1381	24	1.2343	41
1.0460	8	1.1439	25	1.2402	42
1.0518	9	1.1496	26	1.2462	43
1.0575	10	1.1554	27	1.2522	44
1.0632	11	1.1612	28	1.2583	45
1.0690	12	1.1670	29	1.2644	46
1.0747	13	1.1724	30	1.2705	47
1.0805	14	1.1780	31	1.2766	48
1.0862	15	1.1836	32	1.2828	49
1.0920	16	1.1892	33	1.2890	50
1.0977	17	1.1948	34	..	..

TABLE XXII. — SPECIFIC GRAVITY OF SAL-AMMONIAC SOLUTIONS AT 15° C. (59° F.) (GERLACH)

Specific gravity	Percentage NH_4Cl	Specific gravity	Percentage NH_4Cl	Specific gravity	Percentage NH_4Cl
1.00316	1	1.03081	10	1.05648	19
1.00632	2	1.03370	11	1.05929	20
1.00948	3	1.03658	12	1.06204	21
1.01264	4	1.03947	13	1.06479	22
1.01580	5	1.04325	14	1.06754	23
1.01880	6	1.04524	15	1.07029	24
1.02180	7	1.04805	16	1.07304	25
1.02481	8	1.05086	17	1.07575	26
1.02781	9	1.05367	18	1.07658	26.297

TABLE XXIII. — SPECIFIC GRAVITY OF CAUSTIC AMMONIA CONTAINING DIFFERENT QUANTITIES OF NH_3. TEMP. 14° C. (57° F.) (CARIUS)

Specific gravity	Percentage NH_3	Specific gravity	Percentage NH_3	Specific gravity	Percentage NH_3
0.8844	36.0	0.9021	28.2	0.9239	20.4
0.8848	35.8	0.9026	28.0	0.9245	20.2
0.8852	35.6	0.9031	27.8	0.9251	20.0
0.8856	35.4	0.9036	27.6	0.9257	19.8
0.8860	35.2	0.9041	27.4	0.9264	19.6
0.8864	35.0	0.9047	27.2	0.9271	19.4
0.8868	34.8	0.9052	27.0	0.9277	19.2
0.8872	34.6	0.9057	26.8	0.9283	19.0
0.8877	34.4	0.9063	26.6	0.9289	18.8
0.8881	34.2	0.9068	26.4	0.9296	18.6
0.8885	34.0	0.9073	26.2	0.9302	18.4
0.8889	33.8	0.9078	26.0	0.9308	18.2
0.8894	33.6	0.9083	25.8	0.9314	18.0
0.8898	33.4	0.9089	25.6	0.9321	17.8
0.8903	33.2	0.9094	25.4	0.9327	17.6
0.8907	33.0	0.9100	25.2	0.9333	17.4
0.8911	32.8	0.9106	25.0	0.9340	17.2
0.8916	32.6	0.9111	24.8	0.9347	17.0
0.8920	32.4	0.9116	24.6	0.9353	16.8
0.8925	32.2	0.9122	24.4	0.9360	16.6
0.8929	32.0	0.9127	24.2	0.9366	16.4
0.8934	31.8	0.9133	24.0	0.9373	16.2
0.8938	31.6	0.9139	23.8	0.9380	16.0
0.8943	31.4	0.9145	23.6	0.9386	15.8
0.8948	31.2	0.9150	23.4	0.9393	15.6
0.8953	31.0	0.9156	23.2	0.9400	15.4
0.8957	30.8	0.9162	23.0	0.9407	15.2
0.8962	30.6	0.9168	22.8	0.9414	15 0
0.8967	30.4	0.9174	22.6	0.9420	14.8
0.8971	30.2	0.9180	22.4	0.9427	14.6
0.8976	30.0	0.9185	22.2	0.9434	14.4
0.8981	29.8	0.9191	22.0	0.9441	14.2
0.8986	29.6	0.9197	21.8	0.9449	14.0
0.8991	29.4	0.9203	21.6	0.9456	13.8
0.8966	29.2	0.9209	21.4	0.9463	13.6
0.9001	29.0	0.9215	21.2	0.9470	13.4
0.9006	28.8	0.9221	21.0	0.9477	13.2
0.9011	28.6	0.9227	20.8	0.9484	13.0
0.9016	28.4	0.9233	20.6	0.9491	12.8

TABLE XXIII. — SPECIFIC GRAVITY OF CAUSTIC AMMONIA CONTAINING DIFFERENT QUANTITIES OF NH_3. TEMP. 14° (C. 57° F.) (CARIUS) — *Continued*

Specific gravity	Percentage NH_3	Specific gravity	Percentage NH_3	Specific gravity	Percentage NH_3
0.9498	12.6	0.9654	8.4	0.9823	4.2
0.9505	12.4	0.9662	8.2	0.9831	4.0
0.9512	12.2	0.9670	8.0	0.9839	3.8
0.9520	12.0	0.9677	7.8	0.9847	3.6
0.9527	11.8	0.9685	7.6	0.9855	3.4
0.9534	11.6	0.9693	7.4	0.9863	3.2
0.9542	11.4	0.9701	7.2	0.9873	3.0
0.9549	11.2	0.9709	7.0	0.9882	2.8
0.9556	11.0	0.9717	6.8	0.9890	2.6
0.9563	10.8	0.9725	6.6	0.9899	2.4
0.9571	10.6	0.9733	6.4	0.9907	2.2
0.9578	10.4	0.9741	6.2	0.9915	2.0
0.9586	10.2	0.9749	6.0	0.9924	1.8
0.9593	10.0	0.9757	5.8	0.9932	1.6
0.9601	9.8	0.9765	5.6	0.9941	1.4
0.9608	9.6	0.9773	5.4	0.9950	1.2
0.9616	9.4	0.9781	5.2	0.9959	1.0
0.9623	9.2	0.9790	5.0	0.9967	0.8
0.9631	9.0	0.9799	4.8	0.9975	0.6
0.9639	8.8	0.9807	4.6	0.9983	0.4
0.9647	8.6	0.9815	4.4	0.9991	0.2

TABLE XXIV. — SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° C. (59° F.) (KOLB)

Sp. Gr.	Deg. Bé	Deg. Twd.	100 parts by weight correspond to				1 liter contains kilos			
			Per cent		Per cent acid		Chemically pure acid		Acid of 60° Bé	Acid of 50° Bé
			SO_3	H_2SO	of 60° Bé	of 50° Bé	SO_2	H_2SO_4		
1.000	0	..	0.7	0.9	1.2	1.4	0.007	0.009	0.012	0.014
1.007	1	1.4	1.5	1.9	2.4	3.0	0.015	0.019	0.024	0.030
1.014	2	2.8	2.3	2.8	3.6	4.5	0.023	0.028	0.036	0.045
1.022	3	4.4	3.1	3.8	4.9	6.1	0.032	0.039	0.050	0.062
1.029	4	5.8	3.9	4.8	6.1	7.7	0.040	0.049	0.063	0.078
1.037	5	7.4	4.7	5.8	7.4	9.3	0.049	0.060	0.077	0.096
1.045	6	9.0	5.6	6.8	8.7	10.9	0.059	0.071	0.091	0.114
1.052	7	10.4	6.4	7.8	10.0	12.5	0.067	0.082	0.105	0.131
1.060	8	12.0	7.2	8.8	11.3	14.0	0.076	0.093	0.120	0.149
1.067	9	13.4	8.0	9.8	12.6	15.7	0.085	0.105	0.134	0.168
1.075	10	15.0	8.8	10.8	13.8	17.3	0.095	0.116	0.148	0.186
1.083	11	16.6	9.7	11.9	15.3	19.0	0.105	0.129	0.164	0.206
1.091	12	18.2	10.6	13.0	16.7	20.8	0.116	0.142	0.182	0.227
1.100	13	20.0	11.5	14.1	18.1	22.6	0.126	0.155	0.199	0.248
1.108	14	21.6	12.4	15.2	19.5	24.3	0.137	0.168	0.216	0.268
1.116	15	23.2	13.2	16.2	20.7	25.9	0.147	0.181	0.231	0.290
1.125	16	25.0	14.1	17.3	22.2	27.1	0.159	0.195	0.250	0.312
1.134	17	26.8	15.1	18.5	23.7	29.6	0.172	0.210	0.269	0.336
1.142	18	28.4	16.0	19.6	25.1	31.4	0.183	0.224	0.287	0.359
1.152	19	30.4	17.0	20.8	26.6	33.3	0.196	0.239	0.306	0.383
1.162	20	32.4	18.0	22.2	28.4	35.3	0.209	0.258	0.330	0.413
1.171	21	34.2	19.0	23.3	29.8	37.3	0.222	0.273	0.349	0.437
1.180	22	36.0	20.0	24.5	31.4	39.3	0.236	0.289	0.370	0.463
1.190	23	38.0	21.1	25.8	33.0	41.3	0.251	0.307	0.393	0.491
1.200	24	40.0	22.1	27.1	34.7	43.4	0.265	0.325	0.416	0.520
1.210	25	42.0	23.2	28.4	36.4	45.4	0.281	0.344	0.440	0.550
1.220	26	44.0	24.2	29.6	37.9	47.4	0.295	0.361	0.463	0.579
1.231	27	46.2	25.3	31.0	39.7	49.5	0.311	0.382	0.489	0.610
1.241	28	48.2	26.3	32.2	41.2	51.5	0.326	0.400	0.511	0.639
1.252	29	50.4	27.3	33.4	42.8	53.5	0.342	0.418	0.536	0.670
1.263	30	52.6	28.3	34.7	44.4	55.5	0.357	0.438	0.561	0.702
1.274	31	54.8	29.4	36.0	46.1	57.6	0.374	0.459	0.587	0.735
1.285	32	57.0	30.5	37.4	47.9	59.9	0.392	0.481	0.616	0.769
1.297	33	59.4	31.7	38.8	49.7	62.1	0.411	0.503	0.645	0.805
1.308	34	61.6	32.8	40.2	51.5	64.3	0.429	0.526	0.674	0.841
1.320	35	64.0	33.9	41.6	53.3	66.6	0.447	0.549	0.704	0.878
1.332	36	66.4	35.1	43.0	55.1	68.8	0 468	0.573	0.734	0.917
1.345	37	69.0	36.2	44.4	56.9	71.0	0.487	0.597	0.765	0.955
1.357	38	71.4	37.2	45.5	58.3	72.8	0.505	0.617	0.791	0.987
1.370	39	74.0	38.3	46.9	60.0	75.0	0.525	0.642	0.822	1.027
1.383	40	76.6	39.5	48.3	61.9	77.3	0.546	0.668	0.856	1.069
1.397	41	79.4	40.7	49.8	63.8	79.7	0.569	0.696	0.891	1.117
1.410	42	82.0	41.8	51.2	65.6	82.0	0.589	0.722	0.925	1.155

TABLE XXIV. — SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° C. (59° F.) (KOLB) — *Continued*

Sp. Gr.	Deg. Bé	Deg. Twd.	100 parts by weight correspond to				1 liter contains kilos			
			Per cent		Per cent acid		Chemically pure acid		Acid of 60° Bé	Acid of 50° Bé
			SO_3	H_2SO	of 60° Bé	of 50° Bé	SO_2	H_2SO_4		
1.424	43	84.8	42.9	52.6	67.4	84.2	0.611	0.749	0.960	1.198
1.438	44	87.6	44.1	54.0	69.1	86.4	0.634	0.777	0.994	1.243
1.453	45	90.6	45.2	55.4	70.9	88.6	0.657	0.805	1.030	1.288
1.468	46	93.6	46.4	56.9	72.9	91.0	0.681	0.835	1.070	1.336
1.483	47	96.6	47.6	58.3	74.7	93.3	0.706	0.864	1.108	1.382
1.498	48	99.6	48.7	59.6	76.3	95.4	0.730	0.893	1.143	1.429
1.514	49	102.8	49.8	61.0	78.1	97.6	0.754	0.923	1.182	1.477
1.530	50	106.0	51.0	62.5	80.0	100.0	0.780	0.956	1.224	1.530
1.540	51	108.0	52.2	64.0	82.0	102.4	0.807	0.990	1.268	1.584
1.563	52	112.6	53.5	65.5	83.9	104.8	0.836	1.024	1.311	1.638
1.580	53	116.0	54.9	67.0	85.8	107.2	0.867	1.059	1.355	1.694
1.597	54	119.4	56.0	68.6	87.8	109.7	0.894	1.095	1.402	1.752
1.615	55	123.0	57.1	70.0	89.6	112.0	0.922	1.131	1.447	1.809
1.634	56	126.8	58.4	71.6	91.7	114.6	0.954	1.170	1.499	1.872
1.652	57	130.4	59.7	73.2	93.7	117.1	0.986	1.210	1.548	1.936
1.671	58	134.2	61.0	74.7	95.7	119.5	1.019	1.248	1.599	1.996
1.691	59	139.2	62.4	76.4	97.8	122.2	1.055	1.292	1.654	2.037
1.711	60	142.2	63.8	78.1	100.0	125.0	1.092	1.336	1.711	2.118
1.732	61	146.4	65.2	79.9	102.6	127.8	1.129	1.384	1.772	2.284
1.753	62	150.6	66.7	81.7	104.3	130.7	1.169	1.434	1.838	2.294
1.774	63	154.8	68.7	84.1	107.7	134.0	1.219	1.492	1.911	2.387
1.796	64	159.2	70.6	86.5	110.8	138.0	1.268	1.554	1.990	2.416
1.819	65	163.8	73.2	89.7	114.8	143.5	1.332	1.632	2.088	2.671
1.842	66	168.6	81.6	100.0	128.0	149.4	1.523	1.842	2.358	2.872

TABLE XXV. — STRENGTH OF CAUSTIC SODA SOLUTION AT 15° C. (59° F.)

Sp. Gr.	Baumé	Twaddell	Per cent Na_2O	Per cent NaOH	1 cubic meter contains in kilos	
					NA_2O	NaOH
1.007	1	1.4	0.47	0.61	4	6
1.014	2	2.8	0.93	1.20	9	12
1.022	3	4.4	1.55	2.00	16	21
1.029	4	5.8	2.10	2.71	22	28
1.036	5	7.2	2.60	3.35	27	35
1.045	6	9.0	3.10	4.00	32	42
1.052	7	10.4	3.60	4.64	38	49

TABLE XXV. — STRENGTH OF CAUSTIC SODA SOLUTION AT 15° C. (59° F.) — *Continued*

Sp. Gr.	Baumé	Twaddell	Per cent Na_2O	Per cent NaOH	1 cubic meter contains in kilos	
					Na_2O	NaOH
1.060	8	12.0	4.10	5.29	43	56
1.067	9	13.4	4.55	5.87	49	63
1.075	10	15.0	5.08	6.55	55	70
1.083	11	16.6	5.67	7.31	61	79
1.091	12	18.2	6.20	8.00	68	87
1.100	13	20.0	6.73	8.68	74	95
1.108	14	21.6	7.30	9.42	81	104
1.116	15	23.2	7.80	10.06	87	112
1.125	16	25.0	8.50	10.97	96	123
1.134	17	26.8	9.18	11.84	104	134
1.142	18	28.4	9.80	12.64	112	144
1.152	19	30.4	10.50	13.55	121	156
1.162	20	32.4	11.14	14.37	129	167
1.171	21	34.2	11.73	15.13	137	177
1.180	22	36.0	12.33	15.91	146	188
1.190	23	38.0	13.00	16.77	155	200
1.200	24	40.0	13.70	17.67	164	212
1.210	25	42.0	14.40	18.58	174	225
1.220	26	44.0	15.18	19.58	185	239
1.231	27	46.2	15.96	20.59	196	253
1.241	28	48.2	16.76	21.42	208	266
1.252	29	50.4	17.55	22.64	220	283
1.263	30	52.6	18.35	23.67	232	299
1.274	31	54.8	19.23	24.81	245	316
1.285	32	57.0	20.00	25.80	257	332
1.297	33	59.4	20.80	26.83	270	348
1.308	34	61.6	21.55	27.80	282	364
1.320	35	64.0	22.35	28.83	295	381
1.332	36	66.4	23.20	29.93	309	399
1.345	37	69.0	24.20	31.32	326	420
1.357	38	71.4	25.17	32.47	342	441
1.370	39	74.0	26.12	33.69	359	462
1.383	40	76.6	27.10	34.96	375	483
1.397	41	79.4	28.10	36.25	392	506
1.410	42	82.0	29.05	37.47	410	528
1.424	43	84.8	30.08	38.80	428	553
1.438	44	87.6	31.00	39.99	446	575
1.453	45	90.6	32.10	41.41	466	602
1.468	46	93.6	33.20	42.83	487	629
1.483	47	96.6	34.40	44.38	510	658
1.498	48	99.6	35.70	46.15	535	691
1.514	49	102.8	36.90	47.60	559	721
1.530	50	106.0	38.00	49.02	581	750

TABLE XXVI. — REDUCTION OF GAS. VOLUMES TO 0° AND 760 MM.

$$\text{Volume at } 0° \text{ and } 760 \text{ mm.} = v\left(\frac{1}{760\ (1 + .00367t)}\right) \text{ and } (P - p)$$

v = observed volume of gas
t = observed temperature of gas in degrees Centrigade
P = observed barometric pressure, corrected, in millimeters
p = tension of aqueous vapor in millimeters

The logarithm of the volume at 0° and 760 mm. is obtained by adding the logs of v and $\left(\frac{1}{760\ (1 + .00367t)}\right)$ and $(P - p)$.

°C.	Logarithm of $\frac{1}{760(1+.00367t)}$	Tension aqueous vapor mm.	°C.	Logarithm of $\frac{1}{760(1.+00367t)}$	Tension aqueous vapor mm.
0.	3.11919	4.60	5.8	3.11004	6.90
0.2	3.11887	4.65	6.0	3.10973	7.00
0.4	3.11855	4.71	6.2	3.10942	7.09
0.6	3.11824	4.78	6.4	3.10911	7.19
0.8	3.11792	4.85	6.6	3.10880	7.29
1.0	3.11760	4.92	6.8	3.10848	7.39
1.2	3.11728	4.99	7.0	3.10818	7.49
1.4	3.11696	5.06	7.2	3.10786	7.60
1.6	3.11665	5.14	7.4	3.10755	7.70
1.8	3.11633	5.21	7.6	3.10724	7.81
2.0	3.11601	5.29	7.8	3.10693	7.91
2.2	3.11570	5.36	8.0	3.10662	8.02
2.4	3.11538	5.44	8.2	3.10631	8.13
2.6	3.11507	5.52	8.4	3.10600	8.24
2.8	3.11475	5.60	8.6	3.10570	8.36
3.0	3.11443	5.68	8.8	3.10538	8.47
3.2	3.11412	5.76	9.0	3.10508	8.58
3.4	3.11380	5.84	9.2	3.10477	8.70
3.6	3.11349	5.92	9.4	3.10446	8.82
3.8	3.11317	6.00	9.6	3.10415	8.94
4.0	3.11286	6.09	9.8	3.10384	9.06
4.2	3.11255	6.17	10.0	3.10354	9.18
4.4	3.11223	6.26	10.2	3.10323	9.30
4.6	3.11192	6.35	10.4	3.10292	9.43
4.8	3.11160	6.44	10.6	3.10262	9.55
5.0	3.11129	6.53	10.8	3.10231	9.68
5.2	3.11098	6.62	11.0	3.10200	9.81
5.4	3.11067	6.71	11.2	3.10170	9.94
5.6	3.11031	6.81	11.4	3.10139	10.07

TABLE XXVI. — REDUCTION OF GAS. VOLUMES TO 0° AND 760 MM. — *Continued*

°C.	Logarithm of $\frac{1}{760(1+.00367t)}$	Tension aqueous vapor mm.	°C.	Logarithm of $\frac{1}{760(1+.00367t)}$	Tension aqueous vapor mm.
11.6	3.10108	10.21	19.4	3.08932	16.78
11.8	3.10078	10.34	19.6	3.08902	16.98
12.0	3.10047	10.48	19.8	3.08873	17.19
12.2	3.10017	10.62	20.0	3.08843	17.41
12.4	3.09986	10.76	20.2	3.08813	17.62
12.6	3.09956	10.90	20.4	3.08783	17.84
12.8	3.09925	11.04	20.6	3.08754	18.06
13.0	3.09895	11.19	20.8	3.08724	18.28
13.2	3.09864	11.33	21.0	3.08695	18.50
13.4	3.09834	11.48	21.2	3.08665	18.73
13.6	3.09804	11.63	21.4	3.08635	18.96
13.8	3.09773	11.78	21.6	3.08606	19.19
14.0	3.09743	11.94	21.8	3.08576	19.42
14.2	3.09713	12.09	22.0	3.08547	19.66
14.4	3.09682	12.25	22.2	3.08517	19.90
14.6	3.09652	12.41	22.4	3.08488	20.14
14.8	3.09622	12.57	22.6	3.08458	20.39
15.0	3.09592	12.73	22.8	3.08429	20.63
15.2	3.09561	12.89	23.0	3.08400	20.88
15.4	3.09531	13.06	23.2	3.08370	21.14
15.6	3.09501	13.23	23.4	3.08341	21.39
15.8	3.09471	13.39	23.6	3.08312	21 65
16.0	3.09441	13.57	23.8	3.08282	21.91
16.2	3.09411	13.74	24.0	3.08253	22.18
16.4	3.09381	13.91	24.2	3.08224	22.45
16.6	3.09351	14.09	24.4	3.08194	22.72
16.8	3.09321	14.27	24.6	3.08165	22.99
17.0	3.09291	14.45	24.8	3.08136	23.27
17.2	3.09261	14.63	25.0	3.08107	23.55
17.4	3.09231	14.82	25.2	3.08078	23.83
17.6	3.09201	15.00	25.4	3.08048	24.11
17.8	3.09171	15.19	25.6	3.08019	24.40
18.0	3.09141	15.38	25.8	3.07990	24.69
18.2	3.09111	15.58	26.0	3.07961	24.99
18.4	3.09081	15.77	26.2	3.07932	25.28
18.6	3.09051	15.97	26.4	3.07903	25.58
18.8	3.09021	16.17	26.6	3.07874	25.89
19.0	3.08992	16.37	26.8	3.07844	26.19
19.2	3.08962	16.57	27.0	3.07816	26.50

TABLE XXVI. — REDUCTION OF GAS. VOLUMES TO 0° AND 760 MM. — *Continued*

°C.	Logarithm of $\frac{1}{760(1+.00367t)}$	Tension aqueous vapor mm.	°C.	Logarithm of $\frac{1}{760(1+.00367t)}$	Tension aqueous vapor mm.
27.2	3.07787	26.82	31.2	3.07211	33.80
27.4	3.07758	27.13	31.4	3.07182	34.19
27.6	3.07729	27.45	31.6	3.07154	34.58
27.8	3.07700	27.78	31.8	3.07125	34.97
28.0	3.07671	28.10	32.0	3.07097	35.37
28.2	3.07642	28.43	32.2	3.07068	35.77
28.4	3.07613	28.77	32.4	3.07039	36.18
28.6	3.07584	29.10	32.6	3.07011	36.59
28.8	3.07555	29.44	32.8	3.06983	37.01
29.0	3.07527	29.78	33.0	3.06954	37.43
29.2	3.07498	30.13	33.2	3.06926	37.85
29.4	3.07469	30.48	33.4	3.06897	38.28
29.6	3.07440	30.84	33.6	3.06869	38.71
29.8	3.07411	31.19	33.8	3.06841	39.15
30.0	3.07383	31.56	34.0	3.06812	39.59
30.2	3.07354	31.92	34.2	3.06784	40.03
30.4	3.07325	32.29	34.4	3.06756	40.48
30.6	3.07297	32.66	34.6	3.06727	40.93
30.8	3.07268	33.04	34.8	3.06699	41.39
31.0	3.07239	33.42	35.0	3.06671	41.85

TABLE XXVII. — FERROUS SULPHATE AT 15°

GERLACH

Specific gravity	Per cent $FeSO_4$	Per cent $FeSO_4.7H_2O$	Specific gravity	Per cent $FeSO_4$	Per cent $FeSO_4.7H_2O$	Specific gravity	Per cent $FeSO_4$	Per cent $FeSO_4.7H_2O$
1.005	0.565	1	1.0267	2.811	5	1.1430	15.834	25
1.011	1.130	2	1.0537	5.784	10	1.1738	19.622	30
1.016	1.694	3	1.0823	8.934	15	1.2063	23.672	35
1.021	2.258	4	1.1124	12.277	20	1.2391	27.995	40

TABLE XXVIII. — AQUA AMMONIA

W. C. Ferguson

Degrees Baumé	Sp. Gr. $\frac{60°}{60°}$ F.	Per cent NH_3	Degrees Baumé	Sp. Gr. $\frac{60°}{60°}$ F.	Per cent NH_3
10.00	1.0000	.00	19.75	.9349	17.28
10.25	.9982	.40	20.00	.9333	17.76
10.50	.9964	.80	20.25	.9318	18.24
10.75	.9947	1.21	20.50	.9302	18.72
11.00	.9929	1.62	20.75	.9287	19.20
11.25	.9912	2.04	21.00	.9272	19.68
11.50	.9894	2.46	21.25	.9256	20.16
11.75	.9876	2.88	21.50	.9241	20.64
12.00	.9859	3.30	21.75	.9226	21.12
12.25	.9842	3.73	22.00	.9211	21.60
12.50	.9825	4.16	22.25	.9195	22.08
12.75	.9807	4.59	22.50	.9180	22.56
13.00	.9790	5.02	22.75	.9165	23.04
13.25	.9773	5.45	23.00	.9150	23.52
13.50	.9756	5.88	23.25	.9135	24.01
13.75	.9739	6.31	23.50	.9121	24.50
14.00	.9722	6.74	23.75	.9106	24.99
14.25	.9705	7.17	24.00	.9091	25.48
14.50	.9689	7.61	24.25	.9076	25.97
14.75	.9672	8.05	24.50	.9061	26.46
15.00	.9655	8.49	24.75	.9047	26.95
15.25	.9639	8.93	25.00	.9032	27.44
15.50	.9622	9.38	25.25	.9018	27.93
15.75	.9605	9.83	25.50	.9003	28.42
16.00	.9589	10.28	25.75	.8989	28.91
16.25	.9573	10.73	26.00	.8974	29.40
16.50	.9556	11.18	26.25	.8960	29.89
16.75	.9540	11.64	26.50	.8946	30.38
17.00	.9524	12.10	26.75	.8931	30.87
17.25	.9508	12.56	27.00	.8917	31.36
17.50	.9492	13.02	27.25	.8903	31.85
17.75	.9475	13.49	27.50	.8889	32.34
18.00	.9459	13.96	27.75	.8875	32.83
18.25	.9444	14.43	28.00	.8861	33.32
18.50	.9428	14.90	28.25	.8847	33.81
18.75	.9412	15.37	28.50	.8833	34.30
19.00	.9396	15.84	28.75	.8819	34.79
19.25	.9380	16.32	29.00	.8805	35.28
19.50	.9365	16.80			

Specific Gravity determinations were made at 60° F., compared with water at 60° F.

From the Specific Gravities the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = \frac{140}{\text{Sp. Gr.}} - 130.$$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

TABLE XXIX. — ALLOWANCE FOR TEMPERATURE

The coefficient of expansion correction for ammonia solutions, varying with the temperature, must be applied according to the following table:

Corrections to be added for each degree below 60° F.			Corrections to be subtracted for each degree above 60° F.			
Degrees Baumé	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14° Bé	.015° Bé	.017° Bé	.020° Bé	.022° Bé	.024° Bé	.026° Bé
16 "	.021 "	.023 "	.026 "	.028 "	.030 "	.032 "
18 "	.027 "	.029 "	.031 "	.033 "	.035 "	.037 "
20 "	.033 "	.036 "	.037 "	.038 "	.040 "	.042 "
22 "	.039 "	.042 "	.043 "	.045 "	.047 "	
26 "	.053 "	.057 "	.057 "	.059 "		

The Temperature of Products of Combustion is reduced to 18° C. = 64.4° F.

XX	XXI	XXII	XXIII	XXIV	XXV	XXVI
r pound of combustible			Heat of formation at const. pres.			
Products of combustion			Calories per molecular wt. in grammes	B. T. U.		Name of gas or vapor
CO_2	H_2O			Per cu. ft.	Per pound	
....	....	CO − 2.333 +	....	....	....	Carbon, to CO
3.666 +	....	....	....	....	....	Carbon, to CO_2
1.571	....	....	....	+ 138.4	+ 1869.2	Carbonic oxide
....	9.000	....	....	....	....	Hydrogen
2.750	2.250	....	+ 21,750	+ 103.1	+ 2435.6	Methane
2.933	1.800	....	+ 28,560	+ 136.0	+ 1713.6	Ethane
3.000	1.636	....	+ 35,110	+ 167.2	+ 1436.3	Propane
3.034	1.552	....	+ 42,450	+ 202.2	+ 1317.3	Butane
3.055	1.500	....	+ 47,850	+ 227.9	+ 1196.2	Pentane
3.069	1.465	....	+ 61,080	+ 290.9	+ 1278.4	Hexane
3.142	1.286	....	− 2,710	− 12.9	− 174.2	Ethylene
3.142	1.286	....	+ 3,220	+ 15.3	+ 138.0	Propylene
3.142	1.286	....	+ 10,660	+ 50.7	+ 342.6	Butylene
3.142	1.286	....	+ 18,970	+ 113.7	+ 614.1	Amylene
3.384	0.692	....	− 47,770	− 227.5	− 3300.7	Acetylene
3.300	0.900	....	− 39,650	− 188.8	− 1784.2	Allylene
3.259	1.300	....	....	....	....	Crotonylene
3.384	0.692	....	− 12,510	− 47.3	− 229.3	Benzene
3.348	0.782	....	− 3,520	− 16.7	− 68.8	Toluene
3.311	0.849	....	....	....	....	Xylene
3.300	0.900	....	+ 490	+ 2.3	+ 7.3	Mesitylene
3.437	0.563	....	....	....	....	Naphthalene
....	0.529	SO_2 − 1.883	+ 4,740	+ 22.6	+ 250.9	Hydrogen sulphide
....	1.588	N − 0.823	+ 11,890	+ 56.7	+ 1259.0	Ammonia
1.630	0.333	N − 0.518	− 27,480	− 131.1	− 1832.0	Hydrocyanic acid
1.692	....	N − 0.538	− 65,700	− 313.2	− 2273.9	Cyanogen
0.579	....	SO_2 − 1.684	− 26,010	− 124.0	− 616.0	Carbon bi-sulphide
1.375	1.125	....	+ 51,450	+ 246.4	+ 2894.0	Methyl alcohol
1.913	1.174	....	+ 58,470	+ 278.5	+ 2288.0	Ethyl alcohol
....	....	....	....	+ 463.1	+ 3979.1	Carbonic acid
....	....	....	....	+ 327.1	+ 6870.4	Water
....	....	....	....	+ 337.3	+ 1999.1	Sulphur dioxide
....	....	....	....	....	....	Oxygen
....	....	....	....	....	....	Nitrogen
....	....	....	....	....	....	Air

Column VII is from Ganot's "Physics," edition 1896, page 445.
Columns X and XXIII are from Julius Thomsen's "Thermochemical Investigations," and his results are translated into English ts in columns XI–XII and XXIV–XXV.
Columns XIII and XVIII are calculated on the assumption that

air = 20.9% oxygen + 79.1% nitrogen by volume.

air = 23.13% oxygen + 76.87% nitrogen by weight.

(*Facing Page 234*)

TABLE XXXI. — ANALYSIS OF GAS-LIQUOR TAKEN FROM DIFFERENT PARTS OF A WORKS

	From one part of the hydraulic	From another part of the hydraulic	From first air cooler	From second air cooler	From third air cooler	From fourth air cooler	From first washer	From second washer
Color	Muddy orange — turns dark when exposed to air	Same as the first	Clear	Nearly clear	Brown red from tar oil	Dark brown from tar oil	Clear	Clear
Specific Gravity 15.5° C.	1.011	1.012	1.035	1.075	1.115	1.120	1.022	1.010
Ounces by distillation test	6.1	6.0	16.2	36.1	53.0	58.0	16.5	8.3
Ounces by saturation test	2.7	2.8	15.9	35.7	52.5	57.4	16.1	8.1
Ammonium Sulphide—grams per litre	5.20	6.29	34.71	71.43		120.60	22.74	17.43
= NH_3 " " "	2.60	3.14	17.36	35.71		60.30	11.37	8.71
Ammonium Carbonate " " "	8.05	7.29	48.34	116.60		173.23	64.46	24.14
= NH_3 " " "	2.75	1.16	17.14	41.14	112.93	61.43	22.86	8.57
Ammonium Thio-sulphate " " "	1.74	1.17	Trace	1.79	5.03	10.93	3.29	1.93
= NH_3 " " "	0.40	0.27	Trace	0.59	1.16	2.52	0.73	0.44
Ammonium Sulphate " " "	0.11	0.49						
= NH_3 " " "	0.03	0.13						
Ammonium Sulphocyanide " " "	1.60	1.86	0.13	Trace			1.60	0.39
= NH_3 " " "	0.36	0.41	0.03	Trace			0.36	0.09
Ammonium Chloride " " "	22.17	20.79	1.70	2.21	2.87	1.53	1.26	0.54
= NH_3 " " "	7.04	6.60	0.54	0.71	0.91	0.48	0.40	0.17
Ammonium Ferro-cyanide " " "		Trace	0.31	0.59	0.79	5.36		
= NH_3 " " "			0.07	0.14	0.43	1.29		
Total Ammonia — grams per litre	13.19	11.71	35.14	78.29	115.43	126.02	35.72	18.98
Total Fixed Ammonia in per cent	59 %	56 %	1.8 %	1.85 %	2.2 %	3.4 %	4.2 %	4.0 %
Total Ammonia expressed in kilograms per cubic meter of liquor	50	50	131	298	440	479	132	68
Value for Sulphate Production	Very poor	Very poor	Very poor	Very good	Excellent	Excellent	Very good	Insufficient strength

TABLE XXXII. — COMPOSITION OF THE PRINCIPAL FRACTIONS OF COAL TAR

Crude Naphtha. Light Oils (Sp./Gr. less than 1.000) (Distilling below 180° C.)	Dead Oils. Creosote Oils (Sp./Gr. more than 1.000) (Distilling between 180° — 270° C.)	Green or Anthracene Oils (Distilling above 270° C.)	Pitch
Methanes (Paraffins) Tetrane to Decane	Phenol	Methyl-naphthalene Phenanthrene	
Ethenes (Olefines) Pentene to Heptene	Methylphenols	Anthracene	
Ethines (Acetylenes)	Naphthalenes Naphthalene Hydrides	Pyrene Chrysene	
Benzenes Benzene to Durene	Anilines Leucolines	Benzerythrene	
Benzene Hexhydrides	Pyridines	Solid Paraffin	
Naphthalene Hydrides	Quinolines	Benzonitrile	
Phenol (Carbolic Acid)		Carbazol	
Methylphenols (Cresols)		Acridine	
Pyridines			
Sulphur Comp'ds (Thiophenes)			
Amine Derivatives			

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